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Structures, intermolecular rotation barriers, and thermodynamic properties of chlorinated methanols and chlorinated methyl hydroperoxides

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ABSTRACT

STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND THERMODYNAMIC PROPERTIES OF CHLORINATED METHANOLS AND CHLORINATED METHYL HYDROPEROXIDES

by
Hongyan Sun

Thermochemical property data on chlorinated methanols and methyl hydroperoxides are important in oxidation, combustion and atmospheric photochemistry of chlorocarbons. Enthalpy, entropy, and heat capacities are determined for three chlorinated methanols and three chlorinated methyl hydroperoxides using density functional, B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), ab initio QCISD(T)/6-31G(d,p) and the composite CBSQ//B3LYP/6-31G(d,p) calculation methods. Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level. Vibration frequencies are scaled for zero point energies and for thermal corrections. $\Delta H_f^\circ{}_{298}$ are determined at each calculation level using the $\Delta H_{rxn,298}$ with known enthalpies of other reactants and products in each of five different reactions. $S^\circ{}_{298}$ and $C_p(T)$ contributions from vibrations, translations, and external rotations are calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional studies. Potential barriers for internal rotations are calculated at B3LYP/6-31G(d,p) level. Groups for use in Benson type additivity estimations are determined for the carbon with oxygen and chlorine(s). Enthalpy values from the isodesmic reaction show good agreement at all theory levels, suggesting effective cancellation of errors for these two series of molecules.

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To my beloved family

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CHAPTER 1

INTRODUCTION

Chlorocarbons are widely used chemicals as solvents in synthesis and in cleaning agents, as synthesis starting materials and in polymer, pesticide and other product manufacture. Chlorocarbons and other halocarbon compounds are present in the atmosphere from evaporation of these solvents and other anthropogenic activities. They often exhibit relatively long tropospheric lifetimes due to their slow decay or low reaction rates with OH radicals.

Partially chlorinated alkanes undergo initial destruction reactions via loss of a hydrogen atom, (abstraction reaction) usually with OH, while chlorinated or partially chlorinated alkenes and aromatics undergo addition by OH, chlorine atoms or other radicals. These abstraction and addition reactions create chlorocarbon radical intermediates, which further react with oxygen, nitric oxides, and other species to form oxygenated chlorocarbons.

Chlorine atoms are thought to be important reaction initiators in regions near salt-water oceans and other salt-water bodies.[1-3] Initiation reactions of chlorine atoms include rapid abstractions, as well as addition to unsaturated alkenes, aromatics and carbonyls. These chlorine alkyl and adduct radicals will also further react to form oxygenated chlorocarbons.

Chlorine substitution on these methyl and alkyl radicals results in lower reactivity of the radical with O_2. The slower reactions with O_2 permit the chlorinated methyl radical to build up to higher concentrations in combustion environments, relative to CH_3,

and they are more likely to undergo reactions with the radical pool, of which HO_2, OH and O atoms are major species. Associations of CH_2Cl, $CHCl_2$ and CCl_3 with these radicals will form the corresponding chloromethanol or chloromethyl hydroperoxide species.

Thermodynamic property data on these oxygenated chlorocarbon species are needed for evaluation of reaction paths and kinetic processes, including stability of intermediate adducts and prediction of final products. Thermodynamic properties are also needed for use in kinetic modeling and in equilibrium codes. There is very little or no data on thermodynamic properties of these oxygenated chlorocarbons in the literature, with exception of acid carbonyl (acid chloride) species. This thesis is an attempt to estimate fundamental thermodynamic property data on these species using ab initio and density functional calculations.

CHAPTER 2

STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND THERMODYNAMIC PROPERTIESOF CHLORINATED METHANOLS

2.1 Overview

Chlorinated methanols are important intermediates in oxidation, combustion and atmospheric photochemistry of chlorocarbons. Thermochemical property data on these oxy-chlorocarbon species are important in understanding their stability, reaction paths and kinetics. Enthalpy, $\Delta H_f^\circ{}_{298}$, entropy, $S^\circ{}_{298}$ and heat capacities $C_p(T)$ ($300 \leq T/K \leq 1500$) are determined for chloromethanol, dichloromethanol, and trichloromethanol using density functional, B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), ab initio QCISD(T)/6-31G(d,p) and the composite CBSQ//B3LYP/6-31G(d,p) calculation methods (abbreviated as CBSQ//B3**). Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level, with single point calculations for energy at the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3** levels of calculation. Vibration frequencies are scaled for zero point energies and for thermal corrections. Enthalpies of formation ($\Delta H_f^\circ{}_{298}$) are determined at each calculation level using the $\Delta H_{rxn,298}$ with known enthalpies of other reactants and products in each of five different reactions. Standard entropy ($S^\circ{}_{298}$) and heat capacity ($C_p(T)$'s, $300 \leq T/K \leq 1500$) contributions from vibrations, translations, and external rotations are calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional studies. Potential barriers for internal rotations of the hydroxyl group are calculated at B3LYP/6-31G(d,p) level,

and hindered internal rotational contributions to entropy and heat capacity are calculated by summation over the energy levels obtained by direct diagonalizations of the Hamiltonian matrix of hindered internal rotations. Evaluation of data from the reactions, several of which are isodesmic, results in $\Delta H_f^\circ{}_{298}$ values for CH_2ClOH of -58.0±0.5 kcal/mol, $CHCl_2OH$ of -64.4±2 kcal/mol and CCl_3OH of -65.0±2 kcal/mol. Groups for use in Benson type additivity estimations are determined for the carbon with oxygen and chlorine(s). Enthalpy values for the $C/Cl/H_2/O$, $C/Cl_2/H/O$ and $C/Cl_3/O$ groups are -20.1, -26.5, and -27.1 kcal/mol respectively, with error limits as above. Enthalpy values from the isodesmic reaction show good agreement at all theory level, suggesting effective cancellation of errors for this series of molecules.

2.2 Background

A limited number of experimental spectra and ab initio calculations have been reported on chloromethanol, dichloromethanol and trichloromethanol[4-7] and we do not know any experimental determination on enthalpy of formation or combustion. Kunttu et al.[4] reported vibrational frequencies of chloromethanol from infrared spectra, they also calculated the geometry and vibrational frequencies at HF/6-31G(d,p) level for chloromethanol. Tyndall et al.[5] reported experimental infrared frequencies, along with calculated frequencies and geometric parameters at RHF/6-31G(d,p) level for chloromethanol and dichloromethanol. Schneider et al.[6] calculated the structures at RHF/6-3G(d,p) level for these three chlorinated methanols, and also calculated the bond energies and heats of formation at MP2/6-3G(d,p). Melius[7] calculated the structures, moments of inertia, and frequencies at HF/6-3G(d) level of theory, and calculated

enthalpies and free energies for CH_2ClOH, $CHCl_2OH$ and CCl_3OH using BAC-MP4 method.

In this chapter, enthalpy, $\Delta H_f^\circ{}_{298}$, entropy, $S^\circ{}_{298}$ and heat capacities $C_p(T)$ are determined for the chlorinated methanols CH_2ClOH, $CHCl_2OH$ and CCl_3OH using density functional and ab initio calculation methods. Enthalpies of formation are evaluated at each calculation level, using five different working reactions. Contributions to entropy and heat capacity from internal rotation of the hydroxyl group are estimated using direct integration over energy levels of the intramolecular rotation potential energy curve, with B3LYP/6-31G(d,p) level calculations for rotation barrier estimations.

2.3 Computational Methods

2.3.1 Selection of Method

All ab initio calculations are performed using the Gaussian 94 program suite.[8] The structural parameters are fully optimized at B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. The optimized geometrical parameters are used to obtain total electronic energies in B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) single point calculations.[9-11]

B3LYP/6-31G(d,p) is chosen because it is commonly used and is reported to yield accurate geometries and reasonable energies.[12-13] Curtiss et al.[14] reported that B3LYP/6-31G(d,p) provides highly accurate structures for compounds with elements up to atomic number 10. Durant[12,15] has compared density functional calculations BHandH and B3LYP with MP2 and Hartree-Fock methods for geometry and vibration frequencies. He

reports that these density functional methods provide excellent geometries and vibration frequencies, relative to MP2 at a reduced computational expense. Petersson et al.[16] currently recommends use of B3LYP for geometries and frequencies in several of his CBS calculation methods. Comparison of calculation results from B3LYP/6-31G(d,p) against data from higher calculation levels in use of working reaction for $\Delta H_f^\circ{}_{298}$, will provide some calibration of the B3LYP/6-31G(d,p) values with similar working reactions, for larger molecules, where this may be one of the few available calculation methods. B3LYP/6-311+G(3df,2p) is chosen to see if this large basis set results in an improvement to the above commonly used density functional calculation method.[13] QCISD(T)/6-31G(d,p) is a configuration interaction method; but with a small, economical basis set.[17,18] CBSQ calculation is a high level composite method with an empirical correction reported compared with QCISD(T)/6-311+G(3df,2p).[11,19] CBSQ method[20] attempts to approximate the energy of a species at the infinite basis set limit by an extrapolation of the energies of pair natural orbital at the MP2 level. The effects of going from MP2 to QCISD(T) are accounted for with an additivity scheme. The geometry is obtained at the MP2 /6-31G level of theory, while the ZPVE used is the scaled (by 0.9135) HF/6-31G value. For the open-shell systems, there is also a correction for spin contamination in the unrestricted Hartree-Fock wave function. The CBSQ method has been shown to yield reliable $\Delta H_f{}^\circ{}_{298}$ values for small molecules.[20] The CBSQ//B3LYP/6-31G(d,p) method differs from CBSQ in that it employed an improved geometry and ZPVE. The CBSQ//B3LYP/6-31G(d,p) employs geometry optimized at B3LYP/6-31G(d,p) and a ZPVE calculation from scaled (by 0.9806)[21] B3LYP/6-31G(d,p) harmonic vibrational frequencies. This is very similar to the CBS-RAD

method[22] performed by the Radom research group, but has a QCISD(T) calculation in place of CCSD(T). These calculations are referred to as CBSQ//B3** in the present study.

2.3.2 Enthalpies of Formation ($\Delta H_f^\circ{}_{298}$)

Enthalpies of formation ($\Delta H_f^\circ{}_{298}$) for the chlorinated methanols are estimated using total energies obtained by the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculation methods and five reactions, three of which are isodesmic. Total energies are corrected by zero-point vibration energies (ZPVE) which are scaled by 0.9806 as recommended by Scott et al.[21] Thermal correction, 0 K to 298.15 K, is calculated to estimate $\Delta H_f^\circ{}_{298}$ at 298.15 K.[23]

The method of isodesmic reactions relies on the similarity of the bonding environment in the reactants and products that leads to cancellation of systematic errors in the density functional and ab initio molecular orbital calculations[23]. The following five reaction schemes are selected to determine $\Delta H_f^\circ{}_{298}$ of each chlorinated methanol.

$$CH_{3-x}Cl_xOH + CH_4 \rightarrow CH_3OH + CH_{4-x}Cl_x \quad (1)$$

$$CH_{3-x}Cl_xOH + CH_3CH_3 \rightarrow CH_3OH + CH_3CH_{3-x}Cl_x \quad (2)$$

$$CH_{3-x}Cl_xOH + CH_3CH_3 \rightarrow CH_3CH_2OH + CH_{4-x}Cl_x \quad (3)$$

$$CH_{3-x}Cl_xOH + x\ H_2 \rightarrow CH_3OH + x\ HCl \quad (4)$$

$$CH_{3-x}Cl_xOH + x\ H_2O \rightarrow CH_3OH + x\ HOCl \quad (5)$$

The basic requirement of an isodesmic reaction is that the number of each type of bond is conserved in the reaction. Reaction schemes 1, 2, and 3 are isodesmic reactions, and reaction schemes 4 and 5 are not. Reaction schemes 4 and 5 have one (two, three)

added H_2 and H_2O in the reactants and corresponding HCl and HOCl in the products for chloromethanol (dichloromethanol, trichloromethanol). Density functional and ab initio calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and enthalpy of reaction $\Delta H_{rxn}^{\circ}{}_{298}$ is calculated. Since enthalpy of formation of three compounds, have been experimentally determined or theoretically calculated, the unknown enthalpy of formation of CH_2ClOH, $CHCl_2OH$, CCl_3OH are obtained.

Density functional and ab initio calculations at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) level of theory are performed on the most stable conformer of each compound, and the $\Delta H_f{}^{\circ}{}_{298}$ of this conformer are calculated using isodesmic reactions. $\Delta H_f^{\circ}{}_{298}$'s of other conformers, if present, are estimated with the same method. Final $\Delta H_f^{\circ}{}_{298}$ values are from a statistical distribution of rotational conformers.

The AM1[24,25] and PM3[26] methods in the MOPAC 6.0[27] package are used to perform the semi-empirical MO calculations. The enthalpy of formation of three title molecules are calculated with AM1 and PM3 parameters and compared to those obtained from the density functional and ab initio studies at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) level of theory. Direct results from the MOPAC calculations, as well as results from reaction analysis with MOPAC data are presented.

2.3.3 Entropy (S^{o}_{298}) and Heat Capacities ($C_p(T)$'s, $300 \leq T/K \leq 1500$)) and Hindered Rotation Contribution to Thermodynamic Parameters

Entropies S^{o}_{298} and heat capacities ($C_p(T)$'s, $300 \leq T/K \leq 1500$) are calculated using the rigid-rotor-harmonic-oscillator approximation based on frequencies and moments of inertia of the optimized B3LY3/6-31G(d,p) structures. Contributions to entropy and heat capacity from internal rotation of the hydroxyl group are determined using direct integration over energy levels of the intramolecular rotational potential energy. Potential barriers for internal rotations about the C-O bond is determined at the B3LYP/6-31G(d,p) calculation level. A technique for calculation of thermodynamic functions from hindered rotations with arbitrary potentials is used to calculate hindered internal contribution to S^{o}_{298} and $C_p(T)$'s.[28-30] This technique employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix in the basis of wave functions of free internal rotation, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix. In this work, the torsional potential calculated at discrete torsional angles is represented by a truncated Fourier series.

$$V(\Phi) = a_0 + a_i \cos(i\Phi) + b_i \sin(i\Phi) \qquad i = 1, 2, 3, 4, 5 \qquad (2.1)$$

Values of the coefficient a_i are calculated to provide the true minimum and maxima of the torsional potentials with allowance of a shift of the theoretical extreme angular positions.

2.4 Results and Discussion

2.4.1 Geometries and Vibrational Frequencies

The fully optimized geometries at the B3LYP/6-31G(d,p) density functional calculation level for the three chlorinated methanols are presented in Figure 2.1. The numerical

values of the structural parameters including carbon-hydrogen, carbon-chlorine, carbon-oxygen, oxygen-hydrogen bond distance along with applicable bond angles are listed in Table 2.1.

Table 2.1 Geometric Parameters [a] for CH_2ClOH, $CHCl_2OH$, and CCl_3OH

Parameter	CH_3OH	CH_2ClOH [b]	$CHCl_2OH$	CCl_3OH	
	$X_1 = X_2 = H$	$X_1 = H, X_2 = Cl$	$X_1 = H, X_2 = Cl$	$X_1 = X_2 = Cl$	
r (C-X_1)	1.0931	1.0883	1.0863	1.7830	this work [d]
	1.0820	1.0802	1.0726	1.7586	Schneider [e]
r (C-X_2)	1.1007	1.8513	1.8235	1.8252	this work [d]
	1.0883	1.8084	1.7856	1.7844	Schneider [e]
r (C-X_2)	1.1007	1.0934	1.8239	1.8254	this work [d]
	1.0833	1.0756	1.7856	1.7844	Schneider [e]
r (C-O)	1.4174	1.3742	1.3535	1.3512	this work [d]
	1.3984	1.3631	1.3458	1.3441	Schneider [e]
r (O-H)	0.9652	0.9674	0.9702	0.9713	this work [d]
	0.9422	0.9444	0.9466	0.9476	Schneider [e]
∠(O-C-X_1)	106.93	108.18	109.06	107.17	this work [d]
	107.34	112.32	108.69	107.19	Schneider [e]
∠(O-C-X_2)	112.83	112.88	112.42	111.31	this work [d]
	112.14	108.28	111.93	110.79	Schneider [e]
∠(O-C-X_2)	112.83	114.36	112.42	111.31	this work [d]
	112.14	113.46	111.93	110.79	Schneider [e]
∠(H-O-C)	107.75	108.95	109.55	108.92	this work [d]
	109.62	110.59	111.14	110.44	Schneider [e]
∠(X_1-C-O-H)[c]	179.89	67.85	180.19	179.99	this work [d]
	180.00	65.19	180.00	180.00	Schneider [e]

a. Distances in angstroms and angles in degrees. X_1 is the symmetry-unique substituent (H, or Cl) under C_s symmetry; X_2 are the two symmetry equivalent substituents.
b. C_1 symmetry.
c. Dihedral angle between X_1CO and COH planes.
d. Geometrical parameters optimized at the B3LYP/6-31G(d,p) level of theory.
e. Geometrical parameters optimized at RHF/6-31G(d,p) level of theory by Schneider et al.

Effects of chlorine α-substitution on molecular geometries can be seen from Table 2.1. The C-H and O-H bond lengths in the equilibrium conformations of the three title molecules, CH_2ClOH, $CHCl_2OH$, and CCl_3OH optimized at the B3LYP/6-31G(d,p) are essentially invariant, while the C-O bond lengths decrease in order: 1.4174 Å in CH_3OH,

1.3742 Å in CH_2ClOH, 1.3535 Å in $CHCl_2OH$, 1.3512 Å in CCl_3OH. The trends of C-O bond lengths are also observed in the geometries calculated at RHF/6-31G(d) level of theory performed by Schneider et al., which indicate the bond lengths to be 1.3984 Å in CH_3OH, 1.3631 Å in CH_2ClOH, 1.3458 Å in $CHCl_2OH$, 1.3441 Å in CCl_3OH. The interaction between the hydroxyl and methyl groups appears to increase with increasing chlorine substitution based on C-O bond length trends. Differences between the different calculations on the bond lengths of chlorinated methanols are less than 0.03 Å.

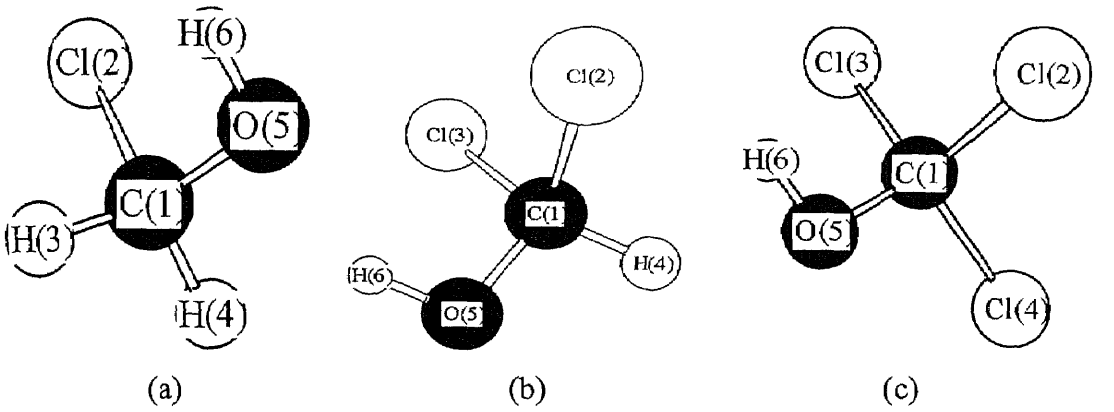


Figure 2.1 B3LYP/6-31G(d,p) optimized geometries of three chlorinated methanols (a) chloromethanol; (b) dichloromethanol; and (c) trichloromethanol.

As illustrated in Figure 2.1 and Table 2.1, the lowest energy conformation for the three title chlorinated methanols is the consistent one with hydroxyl hydrogen gauche to the maximum number of chlorine atoms, despite the obvious steric penalty incurred for adopting such a position. This is because the gauche orientation of the hydrogen group is consistent with a tendency to maximize the interaction between $O\pi_1$ electrons and chlorine atoms[6] and allow for intramolecular H-Cl hydrogen bonding. Harmonic vibrational frequencies are calculated for the three chlorinated methanols at the

B3LYP/6-31G(d,p) level of theory on the basis of optimized geometries at the same level of theory. The vibrational frequencies and moments of inertia for the three chlorinated methanols are given in Tables 2.2 and 2.3. In Table 2.2, one lowest frequency is omitted in calculation of entropies S°_{298} and heat capacities $C_p(T)$, but we replace its contributions with that from internal rotational analysis (see below). Table 2.2 also lists comparisons for the frequencies calculated at the RHF/6-31G(d,p) level performed by Tyndall et al.[5] and infrared frequencies observed by Kunttu et al.[4] and Tyndall et al.[5]

Table 2.2 Vibrational Frequencies [a] (cm^{-1}) for CH_2ClOH, $CHCl_2OH$, and CCl_3OH

Species	ν1[b]	ν2	ν3	ν4	ν5	ν6	ν7	ν8	ν9	ν10	ν11	ν12
CH_2ClOH	349	461	644	969	1138	1203	1352	1411	1522	3077	3182	3803
CH_2ClOH[c]	329	405	647	920	1081	1134	1293	1327	1438	2837	2923	3629
CH_2ClOH[d]	378	466	745	1064	1241	1313	1498	1540	1666	3292	3392	4097
CH_2ClOH[e]	372	469	669	959	1096	1114	1231	1323	1393	2913	2981	3591
CH_2ClOH[f]				959	1083		1318	1374				
$CHCl_2OH$	273	322	447	488	663	694	1157	1124	1281	1415	3194	3174
$CHCl_2OH$[c]	266	311	428	431	652	726	1100	1200	1206	1342	2944	3605
$CHCl_2OH$[f]					1003	1105		1221	1342			
CCl_3OH	227	245	330	342	401	423	524	734	753	1163	1324	3763

a. Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d,p) level of theory.
b. Torsional frequencies. These frequencies are not included in the calculation of entropies S°_{298} and heat capacities $C_p(T)$.
c. Frequencies are calculated at the RHF/6-31G(d,p) level by Tyndall et al. Scaled by 0.87.
d. Nonscaled. Frequencies are calculated at the HF/6-31G(d) level of theory.
e. Infrared frequencies observed by Kunttu et al.
f. Infrared frequencies observed by Tyndall et al.

Table 2.3 Moments of inertia[a] for CH_2ClOH, $CHCl_2OH$, and CCl_3OH

Species	I_a[b]	I_b	I_c
CH_2ClOH	45.86215	330.96314	360.61622
CH_2ClOH[c]	45.24311	316.92910	346.76538
$CHCl_2OH$	267.95397	570.46659	796.29309
CCl_3OH	752.35282	759.41437	1089.13758

a. Optimized at the B3LYP/6-31G(d,p) level of theory.
b. Units in amu-$Bohr^2$.
c. Optimized at the HF/6-31G(d) level of theory.

2.4.2 Enthalpies of Formation ($\Delta H_f^\circ{}_{298}$)

Enthalpies of formation ($\Delta H_f^\circ{}_{298}$) are estimated using total energies and calculated $\Delta H_{rxn,\ 298}$ for the listed reactions. Five reaction schemes, three being isodesmic, calculated $\Delta H_{rxn,\ 298}$ for each reaction and evaluated literature thermodynamic properties for these reference reactants and products are utilized to estimate $\Delta H_f^\circ{}_{298}$ of the target chlorinated methanols. Enthalpies of reaction ($\Delta H_{rxn,\ 298}$) are estimated using total energies obtained by the density functional and ab initio calculations. Zero-point energies (ZPVE's) and thermal correction to 298.15 K are taken into account. The total energies at 298 K at B3LYP/6-31G(d,p), B3LYP/6-311+G(3df+2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculation level, scaled ZPVE's, thermal correction to 298.15 K are listed in Appendix A Table A-1.

For example, one reaction used to calculated $\Delta H_f^\circ{}_{298}$ (CH_2ClOH) is:

$\Delta H_{rxn,\ 298} = \Delta H_f^\circ{}_{298}(CH_3OH) + \Delta H_f^\circ{}_{298}(CH_3Cl) - \Delta H_f^\circ{}_{298}(CH_2ClOH) - \Delta H_f^\circ{}_{298}(CH_4)$

The reaction enthalpies and $\Delta H_f^\circ{}_{298}$'s of the three chlorinated methanols's obtained from use of the reaction schemes are tabulated in Tables 2.4 and 2.5. Enthalpies of formation and uncertainties of reference species from literature which are used to determine the $\Delta H_f^\circ{}_{298}$ values studied in this work are also listed in Appendix Table A-1. Table 2.5 shows that enthalpy of formation of each molecule: CH_2ClOH, $CHCl_2OH$, CCl_3OH at the CBSQ//B3** calculation level throughout all five reaction schemes is almost constant. At the CBSQ//B3** calculation level, $\Delta H_f^\circ{}_{298}$ averaged over five reactions for CH_2ClOH is -58.40±0.73 kcal/mol; $\Delta H_f^\circ{}_{298}$ for $CHCl_2OH$ is -66.09±2.00 kcal/mol; $\Delta H_f^\circ{}_{298}$ for CCl_3OH is -67.10±3.41 kcal/mol, where error values only show the calculated deviations from the five reaction schemes, and do not include experimental errors. The calculation

results for the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and QCISD(T)/6-31G(d,p) calculation levels also result in uniform $\Delta H_f^\circ{}_{298}$ values among three isodesmic reaction schemes. The average $\Delta H_f^\circ{}_{298}$ from three isodesmic reaction schemes at B3LYP/6-31G(d,p) level are -59.36, -66.77, -67.09 kcal/mol for chloromethanol, dichloromethanol, and trichloromethanol respectively. These values are in good agreements (less than ±2 kcal/mol) with the average $\Delta H_f^\circ{}_{298}$ from the higher level CBSQ//B3** calculations (see Table 2.5). This agreement suggests that the economical calculations at B3LYP/6-31G(d,p) level will be accurate for similar alkyl compounds with large number of heavy atoms.

Table 2.4 Reaction Enthalpies at 298K

Reaction Series	B3LYP /6-31G(d,p)	B3LYP /6-311+G(3df,2p)	QCISD(T) /6-31G(d,p)	CBSQ//B3LYP /6-31G(d,p)
1. $CH_2ClOH + CH_4 \rightarrow CH_3OH + CH_3Cl$	9.20	8.29	8.33	8.26
$CHCl_2OH + CH_4 \rightarrow CH_3OH + CH_2Cl_2$	13.67	11.90	13.05	12.91
$CCl_3OH + CH_4 \rightarrow CH_3OH + CHCl_3$	12.13	10.01	12.51	11.58
2. $CH_2ClOH + CH_3CH_3 \rightarrow CH_3OH + CH_3CH_2Cl$	5.21	4.17	3.91	3.26
$CHCl_2OH + CH_3CH_3 \rightarrow CH_3OH + CH_3CHCl_2$	7.80	5.95	5.90	4.43
$CCl_3OH + CH_3CH_3 \rightarrow CH_3OH + CH_3CCl_3$	6.16	4.14	4.26	1.29
3. $CH_2ClOH + CH_3CH_3 \rightarrow CH_3CH_2OH + CH_3Cl$	3.73	3.31	2.77	2.54
$CHCl_2OH + CH_3CH_3 \rightarrow CH_3CH_2OH + CH_2Cl_2$	8.19	6.92	7.48	7.18
$CCl_3OH + CH_3CH_3 \rightarrow CH_3CH_2OH + CHCl_3$	6.66	5.02	6.94	5.85
4. $CH_2ClOH + H_2 \rightarrow CH_3OH + HCl$	-9.80	-12.29	-10.97	-10.46
$CHCl_2OH + 2H_2 \rightarrow CH_3OH + 2HCl$	-25.12	-29.15	-25.46	-23.19
$CCl_3OH + 3H_2 \rightarrow CH_3OH + 3HCl$	-49.04	-53.68	-46.85	-41.95
5. $CH_2ClOH + H_2O \rightarrow CH_3OH + HOCl$	45.76	47.89	46.22	50.21
$CHCl_2OH + 2H_2O \rightarrow CH_3OH + 2HOCl$	86.00	91.20	88.91	98.16
$CCl_3OH + 3H_2O \rightarrow CH_3OH + 3HOCl$	117.64	126.85	124.71	140.08

a. Reaction enthalpies include thermal correction and zero-point energy. Units in kcal/mol. Reaction series 1, 2 and 3 are isodesmic reaction, 4 and 5 are not. No reaction series conserves groups.

Overall results among the four calculation methods appear quite consistent for the three isodesmic reaction series. There is also consistency across reaction series 4, which is not isodesmic, but uses H_2 and HCl for element balance. With the exception of CBSQ//B3** values, enthalpies calculated from use of reaction scheme (5), which is not isodesmic, are not consistent with data from the other four reaction schemes.

Table 2.5 Calculated $\Delta H_f^\circ{}_{298}$ for Chlorinated Methanols [a]

Reaction Series	B3LYP /6-31G(d,p)	B3LYP /6-311+G(3df,2p)	QCISD(T) /6-31G(d,p)	CBSQ /B3LYP**	Error limits[b]
1. $CH_2ClOH + CH_4 \rightarrow CH_3OH + CH_3Cl$	-58.99	-56.37	-58.12	-58.05	±0.24
$CHCl_2OH + CH_4 \rightarrow CH_3OH + CH_2Cl_2$	-66.69	-64.92	-66.07	-65.93	±0.41
$CCl_3OH + CH_4 \rightarrow CH_3OH + CHCl_3$	-66.52	-64.40	-66.90	-65.97	±0.43
2. $CH_2ClOH + CH_3CH_3 \rightarrow CH_3OH + CH_3CH_2Cl$	-59.89	-58.85	-58.59	-57.94	±0.43
$CHCl_2OH + CH_3CH_3 \rightarrow CH_3OH + CH_3CHCl_2$	-66.73	-64.88	-64.83	-63.36	±0.84
$CCl_3OH + CH_3CH_3 \rightarrow CH_3OH + CH_3CCl_3$	-68.01	-65.99	-66.11	-63.14	±0.58
3. $CH_2ClOH + CH_3CH_3 \rightarrow CH_3CH_2OH + CH_3Cl$	-59.21	-58.79	-58.25	-58.02	±0.44
$CHCl_2OH + CH_3CH_3 \rightarrow CH_3CH_2OH + CH_2Cl_2$	-66.90	-65.63	-66.19	-65.89	±0.61
$CCl_3OH + CH_3CH_3 \rightarrow CH_3CH_2OH + CHCl_3$	-66.74	-65.10	-67.02	-65.93	±0.63
4. $CH_2ClOH + H_2 \rightarrow CH_3OH + HCl$	-60.34	-57.85	-59.17	-59.68	±0.10
$CHCl_2OH + 2H_2 \rightarrow CH_3OH + 2HCl$	-67.08	-63.05	-66.74	-69.01	±0.15
$CCl_3OH + 3H_2 \rightarrow CH_3OH + 3HCl$	-65.22	-60.58	-67.41	-72.31	±0.20
5. $CH_2ClOH + H_2O \rightarrow CH_3OH + HOCl$	-53.84	-55.97	-54.30	-58.29	±0.65
$CHCl_2OH + 2H_2O \rightarrow CH_3OH + 2HOCl$	-54.08	-59.28	-56.99	-66.24	±1.25
$CCl_3OH + 3H_2O \rightarrow CH_3OH + 3HOCl$	-45.72	-54.93	-52.79	-68.16	±1.85
Average value for CH_2ClOH[c]:	-59.36±0.47	-58.00±1.41	-58.32±0.24	-58.00±0.06	
Average value for $CHCl_2OH$[c]:	-66.77±0.11	-65.14±0.42	-65.70±0.75	-65.06±1.47	
Average value for CCl_3OH[c]:	-67.09±0.80	-65.16±0.80	-66.68±0.49	-65.01±1.62	

a. Units in kcal/mol. Enthalpy values are reported to 2 decimal places for demonstration of differences between calculation levels; our error analysis shows the values are only accurate to one significant decimal place.
b. Deviations from the uncertainty of enthalpy of formation of reference compounds.
c. Average enthalpy of formation of the calculation and deviations between isodesmic reaction schemes 1, 2, 3.

The CBSQ//B3LYP/6-31G(d,p) and the B3LYP/6-311+G (3d,2p) calculations on CCl_3OH in reaction series (4) and (5) show deviations from data in the isodesmic reaction

schemes, analysis from the reaction $CHCl_2OH + 2H_2O \rightarrow CH_3OH + 2HOCl$, results in consistently high values of $\Delta H_f^\circ{}_{298}$ for $CHCl_2OH$ by the two density functions and the QCISD(T) calculation methods. Deviations for $\Delta H_f^\circ{}_{298}$ across reaction set (5) appear to scale linearly with the coefficient of H_2O and HOCl, suggesting a significant error in calculation of one or both of these species. The CBSQ//B3** values on $CHCl_2OH$ show good agreement in this reaction series (5) with data in all calculation methods for the other reaction sets. We feel this provides good support for accuracy of CBSQ/B3** calculation enthalpies.

There are three staggered conformations in dichloromethanol. Two of them are H-Cl anti conformer and one is H-H anti conformer. The total electronic energies including ZPVE, thermal correction to 298 K and $\Delta H_f^\circ{}_{298}$ of H-Cl anti conformer in $CHCl_2OH$ listed in Appendix A Table A-2 are estimated at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculation levels and three isodesmic reaction schemes. $\Delta H_f^\circ{}_{298}$ of the rotational conformers, their relative fraction (at 298 K), and overall $\Delta H_f^\circ{}_{298}$ of three chlorinated methanols are listed in Table 2.6.

Table 2.6 $H_f^\circ{}_{298}$ for Rotational Conformers, Relative Fraction, and Overall $\Delta H_f^\circ{}_{298}$ [a]

Species	$\Delta H_f^\circ{}_{298}$ (kcal/mol)	Relative fraction	Final $\Delta H_f^\circ{}_{298}$ [c] (kcal/mol)
CH_2ClOH	-58.00	1.0000	-58.00±0.50
$CHCl_2OH(1)$ [b]	-65.06	0.9754	
$CHCl_2OH(2)$ [c]	-62.12	0.0123	-64.42±2.31
CCl_3OH	-65.01	1.0000	-65.01±2.25

a. Enthalpy values are reported to 2 decimal places for demonstration of differences between calculation levels; our error analysis shows the values are only accurate to one significant decimal place.
b. H-H anti conformer in $CHCl_2OH$.
c. H-Cl anti conformer in $CHCl_2OH$.

The B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T), CBSQ//B3LYP/6-31G(d,p) calculations show energy difference values of 3.66, 2.98, 3.11, 2.94 kcal/mol, respectively. Energy difference values at the B3LYP/6-311+G(3df,2p), QCISD(T) and CBSQ//B3LYP/6-31G(d,p) levels show similar data. The average energy difference of these three calculation level values, 3.01 kcal/mol, is taken to calculate the statistical distribution of rotation conformers.

The accuracy of the enthalpies of formation obtained theoretically is controlled by several factors: the level of sophistication (method plus basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and the choice of the working chemical reaction used in the cancellation of calculation errors. The maximum uncertainty in enthalpy values for the reference compounds is listed in Table 2.5 (individual compound uncertainties see Table A-1). CBSQ//B3** appears to be best calculation method based on the results for reaction series (5). We note, however, the averaged deviations in enthalpies from the all calculation levels and the isodesmic reaction schemes are within the error limits of CBSQ//B3** values, as are the known errors of enthalpy on the standards in the working reactions. The ZPVE and thermal correction are also estimated as having a small contribution to the error on relative base. The overall average (using the three isodesmic reactions based on all the four calculation level) $\Delta H_f^\circ{}_{298}$ of CH_2ClOH, $CHCl_2OH$, CCl_3OH are -58.42±1.31 kcal/mol, -65.59± 1.86 kcal/mol, -65.98±1.90 kcal/mol respectively. The $\Delta H_f^\circ{}_{298}$ from the CBSQ//B3** calculation level (using the three isodesmic reactions) for CH_2ClOH, $CHCl_2OH$, CCl_3OH are -58.00±0.50 kcal/mol, -64.42±2.31 kcal/mol, -65.01±2.25 kcal/mol respectively.

Error limits of $\Delta H_f^\circ{}_{298}$ of three chlorinated methanols are obtained by adding the errors inherent in the present computational approach and the uncertainties in the experimental heats of formation.

A comparison of enthalpies of formation calculated using density functional and ab initio theory with the semi-empirical MO methods, AM1 and PM3, is also performed. The results listed in Table B-1 indicate that the PM3 method with isodesmic reaction schemes appears to be a preferred alternative for the calculation of enthalpies of formation for chlorinated methanols among these two semiempirical methods.

2.4.3 Rotational Barriers

Potential barriers for internal rotations of CH_2ClOH, $CHCl_2OH$, and CCl_3OH are calculated at the B3LYP/6-31G(d,p) level. Potential energy as function of dihedral angle is determined by varying the torsion angle at 30° intervals and allowing the remaining molecular structural parameters to be optimized. The geometries at the points of minimum and maximum are fully optimized. The geometries and harmonic vibrational frequencies are calculated for all rotational conformers at B3LYP/6-31G(d,p) level. The barriers for internal rotations are calculated from the differences between the total energy of each conformer and that of the global equilibrium, where the zero-point vibrational energy (ZPVE) and thermal correction to 298 K are also included. Total energies at 0 K, ZPVE, and thermal correction to 298 K and calculated rotation barriers for each rotational conformer of the three chlorinated methanols are listed in Table C-1. Potential energy vs. torsion angle diagrams for internal rotations about C-O bond of the three chlorinated methanols are shown in Figures 2.2, 2.3, and 2.4. Points are calculated values

at B3LYP/6-31G(d,p) level. Lines are results of the Fourier expansion. The values of the coefficients of the Fourier expansion, a_i and b_i in equation (2.1) are listed in Table 2.7.

Table 2.7 Coefficients of Truncated Fourier Series Representation Expansions

species	a_0	a_1	a_2	a_3	a_4	a_5
CH_2Cl-OH	2.650	-1.782	1.860	0.764	0.011	0.046
$CHCl_2$-OH	3.295	-0.795	0.488	0.854	-0.025	0.032
CCl_3-OH	0.883	-0.004	0.007	0.912	-0.001	0.007
		b_1	b_2	b_3	b_4	b_5
CH_2Cl-OH		0.000	0.000	0.000	0.000	0.000
$CHCl_2$-OH		-1.456	-0.736	0.054	-0.035	-0.035
CCl_3-OH		0.000	0.000	0.000	0.000	0.000

a. Units in kcal/mol. Values of rotation barriers calculated at B3LYP/6-31G(d,p) level are used to calculate the coefficients.

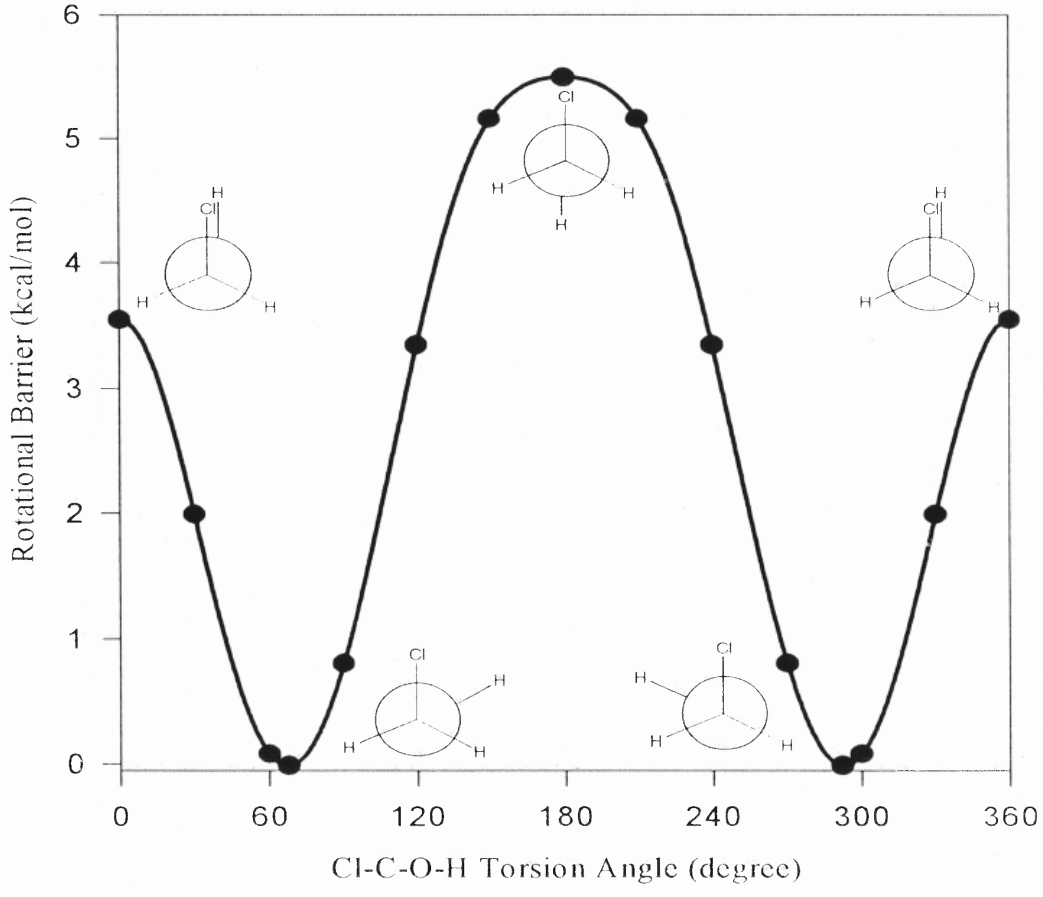


Figure 2.2 Potential barriers for internal rotation about C-O bond of CH_2ClOH. Points are calculated values at B3LYP/6-31G(d,p) level of theory. Line is Fourier expansion, with the coefficients listed in Table 2.6.

Figure 2.2 shows the calculated rotational barrier for chloromethanol. The H-Cl gauche conformer is the most stable conformer. The H-Cl eclipsed conformer, which has a rotational barrier of 3.56 kcal/mol, is more stable than the H-Cl anti conformer which has the highest rotational barrier, 5.50 kcal/mol. This is because the H-Cl anti conformer has two non-bonding electron pairs from the oxygen atom close to the Cl atom. The H-Cl eclipsed conformer has two non-bonding electron pairs close to two H atoms, and the H-Cl gauche conformer has only one non-bonding electron pair close to the Cl atom.

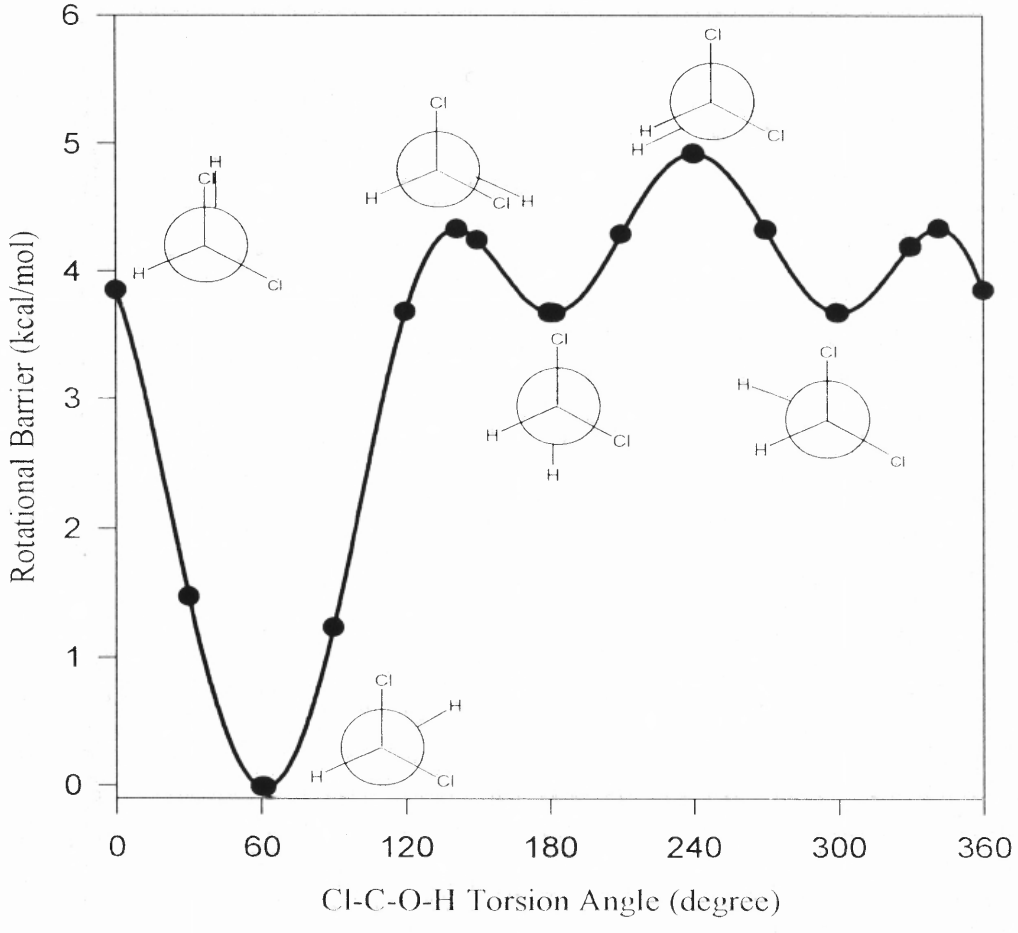


Figure 2.3 Potential barriers for internal rotation about C-O bond of $CHCl_2OH$. Points are calculated values at B3LYP/6-31G(d,p) level of theory. Line is Fourier expansion, with the coefficients listed in Table 2.6.

Figure 2.3 shows calculated rotational barriers in dichloromethanol. The H-H eclipsed conformer has a slightly higher rotational barrier, 4.94 kcal/mol, than that of the H-Cl eclipsed conformer which has a rotational barrier of 4.32 kcal/mol. This is because in the H-H eclipsed conformer both non-bonding election pairs are eclipsed with two Cl atoms. The H-H anti conformer is more stable than the H-Cl anti conformer, this is because the H-H anti conformer has two chlorine interactions with the oxygen atom non-bonding electron pair and the H-Cl anti conformer has three chlorine gauche interactions with the oxygen atom non-bonding electron pair. Results for this analysis indicate a gauche interaction between the Cl atom and the O atom non-bonding electron pair increases the energy by 3.68 kcal/mol.

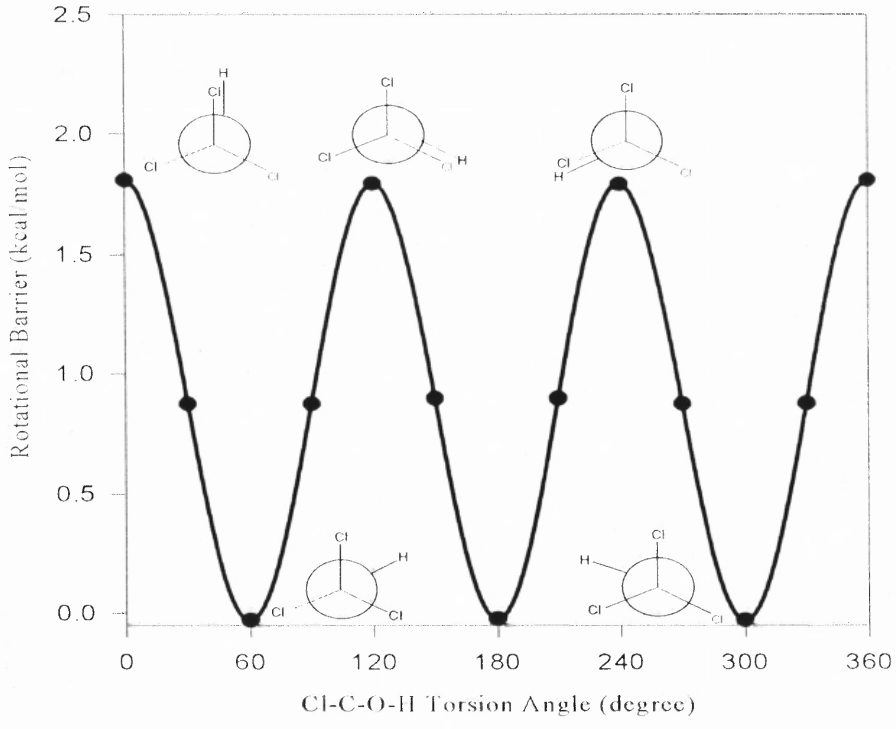


Figure 2.4 Potential barriers for internal rotation about C-O bond of CCl_3OH. Points are calculated values at B3LYP/6-31G(d,p) level of theory. Line is Fourier expansions with the coefficients listed in Table 2.6.

Figure 2.4 shows the calculated symmetric rotational barrier for tri-chloromethanol. The calculation shows that the H-Cl eclipsed conformer has a rotational barrier of 1.82 kcal/mol above the H-Cl gauche conformer, which is the most stable conformer. Three chlorine atoms on the methyl make the rotation about the C-O bond symmetric, and all stable conformers have four chlorine gauche interactions with oxygen non-bonded electron pairs, while this molecule has the lowest barrier among three chlorinated methanols, this probably results from increased strain (repulsion) in the stable conformers.

2.4.4 Entropy (S^{o}_{298}) and Heat Capacity ($C_p(T)$'s ($300 \leq T/K \leq 1500$))

S^{o}_{298} and $C_p(T)$'s calculation results using B3LYP/6-31G(d,p) determined geometries and frequencies are summarized in Table C-1. TVR, represents the sum of the contributions from translations, external rotations and vibrations for S^{o}_{298} and $C_p(T)$'s. The torsion frequency calculated for the internal rotor is not included in TVR. Instead, a more exact contribution from hindered rotations is calculated. I.R., represent the contributions from internal rotation about C-O bond for S^{o}_{298} and $C_p(T)$'s. Final standard entropies also include correction from rotational conformers. This correction is calculated by the following formula for 1 mole of mixture[35]:

$$\Delta S_{mixing} = -R \sum n_i \ln (n_i) \qquad (2.2)$$

where n_i is the equilibrium mole fraction of the *i*th form. ΔS_{mixing} represents the entropy of mixing of rotational conformations or optical conformations.

Table C-1 also lists comparisons with previous ab initio calculation data. The calculation results show good agreement for the entropies with data reported by Schneider

et al [6] for CH_2ClOH and $CHCl_2OH$ and also for the enthalpy, entropy and heat capacities of $CHCl_2OH$, CCl_3OH with data calculated by Melius.[33] We have checked the geometry of CH_2ClOH on the web site of Carl Melius[7] and find that the Cl-C-O-H dihedral angle of CH_2ClOH is 180 degrees which is different from the optimized geometry in this work. In the geometry of Melius's, CH_2ClOH has the hydroxyl H atom trans to Cl atom, but oxygen lone pairs gauche to the Cl atom, corresponds to the maximum in our intramolecular rotation potential energy curve (see Fig.2.2). This is probably the reason why the enthalpy of CH_2ClOH calculated by Melius is 2.98 kcal/mol higher than that calculated in this work. A separate calculation of CH_2ClOH geometry optimized at HF/6-31G(d,p) level of theory results in similar frequencies and moments of inertia in agreements with that optimized at B3LYP/6-31G(d,p) level of theory (see Table 2.2 and Table 2.3). The close agreement in frequencies and moments of inertia results in good agreement with the entropy (S°_{298}) and heat capacities $C_p(T)$ of CH_2ClOH estimated in this work.

2.4.5 Group Additivity Values

The group additivity method,[35] is an easy, and reasonably accurate calculation for hydrocarbons and oxygenated hydrocarbons,[36] modifications have also been reported that make it useful for chlorinated and fluorinated hydrocarbons.[29,30,37,38] In this work, we develop a set of chloro-oxy hydrocarbon groups derived from the thermodynamic property data of three chlorinated methanols. Values are reported for the groups $C/Cl/H_2/O$, $C/Cl_2/H/O$, $C/Cl_3/O$ derived from CH_2ClOH, $CHCl_2OH$, and CCl_3OH respectively. $\Delta H_f^\circ{}_{298}$ and C_P's of $C/Cl/H_2/O$ are calculated on the basis of

$$(CH_2ClOH) = (C/Cl/H_2/O) + (O/C/H)$$

S°_{298} of $C/Cl/H_2/O$ is calculated on the basis of

$$(CH_2ClOH) = (C/Cl/H_2/O) + (O/C/H) + R\ln(\sigma)$$

Where R = 1.987 cal/mol K, and σ is symmetry number, which is 3 for CCl_3OH and CH_3OH. The group values of $C/Cl_2/H/O$, $C/Cl_3/O$ are estimated in the same manner. Selection of the initial group values is critical to development of group additivity for accurate property estimation, these criteria are fully discussed in references 36 and 37. The group values for $\Delta H_f^{\circ}{}_{298}$, S°_{298}, and C_p (T) of O/C/H are taken from the existing literature values[36] which come from alcohols. The carbon-chlorine-oxygen group values are derived in this work are listed in Table 2.8. Table 2.8 shows that group values for heat of formation decrease with increased number of chlorines but not in a linear progression. The non-linearity probably results from increased numbers of gauche chlorine-oxygen non-bond electron pair interactions. The carbon-chlorine-oxygen group value for entropies and heat capacities below 1500 K increase with increased number of chlorines as expected for the increased mass and lower vibrational frequencies.

Table 2.8 Group Values

Groups	$\Delta H_f^{\circ}{}_{298}$[a]	S°_{298}[b]	Cp300[b]	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
O/C/H[c]	-37.90	29.07	4.30	4.50	4.82	5.23	6.02	6.61	7.44
$C/Cl/H_2/O$	-20.10	36.55	8.88	11.18	13.02	14.35	16.09	17.27	19.19
$C/Cl_2/H/O$	-26.52	41.77	12.61	15.71	17.73	18.80	19.62	19.94	20.60
$C/Cl_3/O$	-27.11	50.54	16.34	18.45	19.65	20.28	20.82	21.06	21.46

a. Units in kcal/mol. Units in cal/mol-K.
b. Reference 36.

2.5 Summary

Thermodynamic Properties of three chlorinated methanols are calculated using density functional and ab initio methods with five reaction schemes for cancellation of errors.

Standard enthalpy of formation, $\Delta H_f^\circ{}_{298}$ are calculated using isodesmic reaction schemes based on B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) levels and include the statistical distribution of rotational conformers. CBSQ//B3LYP/6-31G(d,p) calculation values of $\Delta H_f^\circ{}_{298}$ do not show the large deviations for non isodesmic reactions, that are observed in the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) calculations. Entropies $S^\circ{}_{298}$ and heat capacities ($C_p(T)$'s ($300 \leq T/K \leq 1500$)) are determined by B3LYP/6-31G(d,p) optimized geometries and frequencies. Enthalpy, entropy and $C_p(T)$ properties are determined for $C/Cl/H_2/O$, $C/Cl_2/H/O$, and $C/Cl_3/O$ chloro-oxy groups, which are additivity groups for oxygenated chlorocarbons.

CHAPTER 3

STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND THERMODYNAMIC PROPERTIES OF CHLORINATED METHYL HYDROPEROXIDES

3.1 Overview

Chlorinated methyl hydroperoxides are important intermediates in oxidation, combustion and atmospheric photochemistry of chlorocarbons. Thermochemical property data on these oxy-chlorocarbon species are important to understanding their stability, reaction paths and kinetics. Enthalpy, $\Delta H_f^\circ{}_{298}$, entropy, $S^\circ{}_{298}$ and heat capacities $C_p(T)$ ($300 \leq T/K \leq 1500$) are determined for chloro-methyl-hydroperoxide, dichloro-methyl-hydroperoxide, and trichloro-methyl-hydroperoxide using density functional B3LYP/6-31g(d,p), and B3LYP/6-311+G(3df,2p), ab initio QCISD(T)/6-31G(d,p) and the composite CBSQ//B3LYP/6-31G(d,p) calculation methods (abbreviated as CBSQ//B3**). Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) density functional calculation level, with single point calculations for energy at the B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) levels of calculation. Vibration frequencies are scaled for zero point energies and for thermal corrections. Enthalpies of formation ($\Delta H_f^\circ{}_{298}$) are determined at each calculation level using the $\Delta H^\circ{}_{rxn,298}$ with known enthalpies of other reactants and products in each of five different reactions. Standard entropy ($S^\circ{}_{298}$) and heat capacity ($C_p(T)$'s, $300 \leq T/K \leq 1500$) contributions from vibrations, translations, and external rotations are calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional studies.

Potential barriers for internal rotations are calculated at B3LYP/6-31G(d,p) level, and hindered internal rotational contributions to entropy and heat capacity are calculated by summation over the energy levels obtained by direct diagonalizations of the Hamiltonian matrix of hindered internal rotations. Evaluation of data from the reactions, several of which are isodesmic, results in $\Delta H_f^\circ{}_{298}$ values for CH_2ClOOH of -41.4±1kcal/mol, $CHCl_2OOH$ of -44.7±3 kcal/mol and CCl_3OOH of -45.1±3 kcal/mol, and suggests that intramolecular hydrogen bonding decreases enthalpy values by several kcal/mol in each. Groups for use in Benson type additivity estimations are determined for the carbon with oxygen and chlorine(s). Enthalpy values for the $C/Cl/H_2/OO$, $C/Cl_2/H/OO$ and $C/Cl_3/OO$ groups are -17.9, -21.2, and -21.6 kcal/mol respectively with error limits as above. Enthalpy values from the isodesmic reaction show good agreement at all theory levels, suggesting effective cancellation of errors in these reaction sets. CBSQ//B3** calculations are judged to be the most accurate in this study, especially for non-isodesmic reaction systems.

3.2 Background

Alkyl hydroperoxides are important intermediates in low-temperature combustion processes, such as in the initial stages of combustion[41,42] and in the atmospheric photochemical oxidation of hydrocarbons.[43,44] Chlorinated alkyl hydroperoxides pay a similar role in the oxidation of chlorinated hydrocarbons. Knowledge of the thermodynamic parameters for these species is central to understanding and predicting reaction pathways, rate constants and equilibrium constants. There are few experimental studies on the thermodynamic properties of chlorinated alkyl hydroperoxides. One

reason for this is the difficulty in accurate determination of structures because of strong influences of intramolecular and intermolecular forces in the condensed phase. Rapid interconversion of conformers and the instability of alkyl hydroperoxides leads to complexities in studies of these species.

Experimental studies on heats of formation ($\Delta H_f^\circ{}_{298}$) of few alkyl hydroperxides have been reported. Experimental values of $\Delta H_f^\circ{}_{298}$ are available for HOOH (-32.5 kcal/mol),[45] C_2H_5OOH (-47.6 kcal/mol),[46] i-C_3H_7OOH (-65.0 kca/mol),[46] t-C_4H_9OOH (-58.8 kcal/mol),[47] and several cycloalkylhydroperoxides. Knyazev et al.[48] estimated the enthalpy of formation of chlorinated alkyl hydroperoxides using their experimental data on the peroxy radicals and on the assumed hydrogen bond enthalpy. They reported that enthalpy of formation for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH are -36.59±3.97, -39.96±3.39, -40.37±2.84 kcal/mol respectively. Lay et al.[28] calculated internal rotation barriers, vibrational frequencies, and thermodynamic properties of α-chlorinated ethyl hydroperoxides at HF/6-31G* and MP2/6-31G* calculation levels.

In this chapter, enthalpy, $\Delta H_f^\circ{}_{298}$, entropy, $S^\circ{}_{298}$ and heat capacities $C_p(T)$ are determined for the chlorinated methyl hydroperoxides CH_2ClOOH, $CHCl_2OOH$ and CCl_3OOH using density functional and ab initio calculation methods. Enthalpies of formation are evaluated at each calculation level, using five different working reactions. Contributions to entropy and heat capacity from internal rotation are estimated using direct integration over energy levels of the intramolecular rotation potential energy curve, with B3LYP/6-31G(d,p) level calculations for rotation barrier estimations.

3.3 Computational Methods

3.3.1 Enthalpies of Formation ($\Delta H_f^\circ{}_{298}$)

Enthalpies of formation ($\Delta H_f^\circ{}_{298}$) for the chlorinated methyl hydroperoxides are estimated using total energies obtained by the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculation methods and five reactions, three of which are isodesmic. Total energies are corrected by zero-point vibration energies (ZPVE) which are scaled by 0.9806 as recommended by Scott et al.[21] Thermal correction, 0 K to 298.15 K, is calculated to estimate $\Delta H_f^\circ{}_{298}$ at 298.15 K.[23]

The method of isodesmic reactions relies on the similarity of bonding environments in the reactants and products that leads to cancellation of systematic errors in the density functional and ab initio molecular orbital calculations[23]. The following reactions are selected to determine $\Delta H_f^\circ{}_{298}$ of each chlorinated methylhydroperoxide.

$$CH_{3-x}Cl_xOOH + CH_4 \rightarrow CH_3OOH + CH_{4-x}Cl_x \quad (1)$$

$$CH_{3-x}Cl_xOOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CH_{3-x}Cl_x \quad (2)$$

$$CH_{3-x}Cl_xOOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_{4-x}Cl_x \quad (3)$$

$$CH_{3-x}Cl_xOOH + x\ H_2 \rightarrow CH_3OOH + x\ HCl \quad (4)$$

$$CH_{3-x}Cl_xOOH + x\ H_2O \rightarrow CH_3OOH + x\ HOCl \quad (5)$$

The basic requirement of an isodesmic reaction is that the number of each type of bond is conserved in the reaction. Reaction schemes 1, 2, and 3 are isodesmic reactions, and reaction schemes 4 and 5 are not. Reaction schemes 4 and 5 have one (two, three) added H_2's (for 4) and H_2O's (for 5) in reactants and corresponding HCl's and HOCl's in products, for the respective chloromethyl-, (dichloromethyl-, trichloromethyl-) hydroperoxides. Density functional and ab initio calculations with ZPVE and thermal

correction are performed for all four compounds in each reaction, and enthalpy of reaction $\Delta H^{\circ}_{rxn,298}$ is calculated. Since enthalpy of formation of the three compounds, have been experimentally determined or theoretically calculated, the unknown enthalpy of formation of CH_2ClOOH, $CHCl_2OOH$, CCl_3OOH are obtained.

Density functional and ab initio calculations at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3** level of theory are performed on the most stable conformer of each compound, and the $\Delta H_f^{\circ}{}_{298}$ of this conformer is calculated using isodesmic reactions. $\Delta H_f^{\circ}{}_{298}$'s of other conformers, if present, are estimated with the same method. Final $\Delta H_f^{\circ}{}_{298}$ values are from a statistical distribution of rotational conformers.

The AM1[24,25] and PM3[26] methods in the MOPAC 6.0[27] package are used to perform the semiempirical MO calculations. The enthalpy of formation of three title molecules are calculated with AM1 and PM3 parameters and compared to those obtained from the density functional and ab initio studies. Direct results from the MOPAC calculations, as well as results from reaction analysis with MOPAC data are presented.

3.3.2 Entropy (S°_{298}) and Heat Capacities ($C_p(T)$'s, $300 \leq T/K \leq 1500$)) and Hindered Rotation Contribution to Thermodynamic Parameters

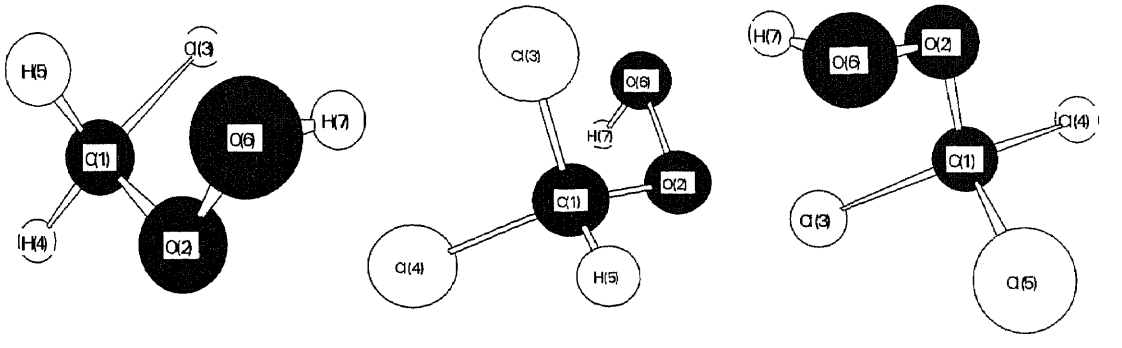
Entropies S°_{298} and heat capacities ($C_p(T)$'s, $300 \leq T/K \leq 1500$) are calculated using the rigid-rotor-harmonic-oscillator approximation based on frequencies and moments of inertia of the optimized BLY3/6-31G(d,p) structures. Contributions to entropy and heat capacity from internal rotation are determined using direct integration over energy levels of the intramolecular rotational potential energy. Potential barriers for internal rotations

about the C-O and O-O bonds are determined at the B3LYP/6-31G(d,p) calculation level. A technique for calculation of thermodynamic functions from hindered rotations with arbitrary potentials is used to calculate hindered internal contributions to S°_{298} and $C_p(T)$'s.[28-30] This technique employs expansion of the hindrance potential in the Fourier series, calculation of the Hamiltonian matrix in the basis of wave functions of free internal rotation, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix. In this chapter, the torsional potential calculated at discrete torsional angles is represented by a truncated Fourier series. Values of the coefficients a_i and b_i are calculated to provide the minimum and maxima of the torsional potentials with allowance of a shift of the theoretical extreme angular positions.

3.4 Results and Discussion

3.4.1 Geometries and Vibrational Frequencies

The fully optimized geometries at the B3LYP/6-31g(d,p) density functional calculation level for the three chlorinated methyl hydroperoxides are presented in Figure 3.1.



(a) (b) (c)

Figure 3.1 B3LYP/6-31G(d,p) optimized geometries of three chlorinated methyl hydroperoxides (a)chloromethylhydroperoxide; (b) dichloromethylhydroperoxide; and (c) trichloromethylhydroperoxide.

The numerical values of the structural parameters including carbon-hydrogen, carbon-chlorine, carbon-oxygen, oxygen- oxygen, oxygen-hydrogen bond distances along with applicable bond angles are listed in Table 3.1. The calculation at the B3LYP/6-31g(d,p) level gives O-O bond length 1.450 Å, is in good agreement with the experimental data (1.452 Å) by Khachkuruzov and Przhevalskii [49] using IR spectroscopy. Effects of chlorine α-substitution on molecular geometries can be seen from Table 3.1. The C-H, O-O and O-H bond lengths in the equilibrium conformations of three title molecules, CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH optimized at the B3LYP/6-31G(d,p) are essentially invariant, while the C-O bond lengths decrease 0.04 Å for the first choro substitution, then remain near constant. The interaction between the hydroperoxide and methyl groups appears to increase with the chlorine substitution based on C-O bond length trends.

Table 3.1 Geometry Parameters[a] for CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH

Parameter	CH_3OOH $X_3=X_4=X_5=H$	CH_2ClOOH $X_3=Cl, X_4=X_5=H$	$CHCl_2OOH$ $X_3=X_4=Cl, X_5=H$	CCl_3OOH $X_3=X_4=X_5=Cl$
r (C_1-O_2)	1.4168	1.3774	1.3702	1.3799
r (C_1-X_3)	1.0977	1.8422	1.7967	1.8177
r (C_1-X_4)	1.0946	1.0903	1.8200	1.7842
r (C_1-X_5)	1.0961	1.0897	1.0893	1.7941
r (O_2-O_6)	1.4566	1.4494	1.4456	1.4466
r (O_6-H_7)	0.9713	0.9742	0.9748	0.9752
∠(O_2-C_1-X_3)	111.8619	112.6811	113.9688	111.0730
∠(O_2-C_1-X_4)	104.5995	105.9822	112.1017	103.0123
∠(O_2-C_1-X_5)	109.6959	106.7114	104.7546	110.1259
∠(X_3-C_1-X_4)	111.4720	112.5236	110.2574	112.6700
∠(X_3-C_1-X_5)	109.5383	105.7827	108.1073	109.0470
∠(X_4-C_1-X_5)	109.5542	113.1406	107.2074	110.8051
∠(C_1-O_2-O_6)	106.0986	107.9261	110.3723	109.4487
∠(O_2-O_6-H_7)	99.8517	100.4437	100.4066	100.3041
∠(X_3-C_1-O_2-O_6)	64.0775	75.9617	-60.8432	63.4080
∠(X_4-C_1-O_2-O_6)	-177.2522	-167.6866	65.2787	-178.7192
∠(X_5-C_1-O_2-O_6)	-58.9504	-43.5395	-178.8003	-59.2732
∠(C_1-O_2-O_6-H_7)	-115.0951	-95.2057	-93.6719	-96.3122

a. Distances in angstroms and angles in degrees.

As illustrated in Figure 3.1 and Table 3.1, the lowest energy conformation for the three title chlorinated hydroperoxides is the one consistent with the hydroxyl oxygen gauche to the maximum number of chlorine atoms, despite the obvious steric penalty incurred for adopting such a position. This is because the gauche orientation of the hydroxyl group is consistent with a tendency to maximize the interaction between $O\pi_1$ electrons and chlorine atoms[6] and allow for intramolecular H-Cl hydrogen bonding.

Harmonic vibrational frequencies are calculated for the three chlorinated methyl hydroperoxides at the B3LYP/6-31G(d,p) level of theory on the basis of optimized geometries at the same level of theory. The vibrational frequencies and moments of inertia for the three chlorinated methyl hydroperoxides are given in Tables 3.2 and 3.3.

Table 3.2 Vibrational Frequencies [a] (cm^{-1})

Species	ν1[b]	ν2[b]	ν3	ν4	ν5	ν6	ν7	ν8	ν9	ν10	ν11	ν12	ν13	ν14	ν15
CH_2ClOOH	151	267	368	497	668	885	1002	1103	1275	1341	1399	1465	3106	3192	3723
$CHCl_2OOH$	144	225	243	294	402	556	726	771	901	1085	1227	1332	1413	3164	3178
CCl_3OOH	147	201	238	258	276	333	404	436	548	766	857	932	1056	1410	3712

a. Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d,p) level of theory.
b. R--OOH and RO--OH torsional frequencies; these frequencies are not included in the calculation of entropies S°_{298} and heat capacities $C_p(T)$.

Table 3.3 Moments of inertia [a]

	I_a[b]	I_b	I_c
CH_2ClOOH	124.2324	523.8976	600.9131
$CHCl_2OOH$	533.0179	638.9753	1000.159
CCl_3OOH	945.1712	1098.188	1239.275

a. Optimized at the B3LYP/6-31G(d,p) level of theory.
b. Units in amu-$Bohr^2$.

In Table 3.2, the two lowest frequencies (corresponding to torsional motion) are omitted in calculation of entropies S°_{298} and heat capacities $C_p(T)$, but we replace their contributions with that from internal rotation analysis.

3.4.2 Enthalpies of Formation ($\Delta H_f^\circ{}_{298}$)

Enthalpies of formation ($\Delta H_f^\circ{}_{298}$) are estimated using total energies and calculated $\Delta H^\circ{}_{rxn,298}$ for the listed reactions. Five reaction schemes, three being isodesmic, calculated $\Delta H^\circ{}_{rxn,298}$ for each reaction and evaluated literature thermodynamic properties for these reference reactants and products are utilized to estimate $\Delta H_f^\circ{}_{298}$ of the target chlorinated methyl hydroperoxides. Enthalpies of reaction ($\Delta H^\circ{}_{rxn,298}$) are estimated using total energies obtained by the density functional and ab initio calculations. Zero-point energies (ZPVE's) and thermal correction to 298.15 K are taken into account. The total energies at 298 K at B3LYP/6-31G(d,p), B3LYP/6-311+G(3df+2p), QCISD(T)/6-31G(d,p) and CBSQ//B3** calculation level, scaled ZPVE's, thermal correction to 298.15 K are listed in Table A-1.

As an example, one reaction used to calculated $\Delta H_f^\circ{}_{298}$ (CH_2ClOOH) is:

$$\Delta H^\circ{}_{rxn,\,298} = \Delta H_f^\circ{}_{298}(CH_3OOH) + \Delta H_f^\circ{}_{298}(CH_3Cl) - \Delta H_f^\circ{}_{298}(CH_2ClOOH) - \Delta H_f^\circ{}_{298}(CH_4)$$

The reaction enthalpies and $\Delta H_f^\circ{}_{298}$'s of the three chlorinated methyl hydroperoxides's obtained from use of the reaction schemes are tabulated in Tables 3.4 and 3.5. Enthalpies of formation and uncertainties of reference species (data from literature) which are used to determined $\Delta H_f^\circ{}_{298}$ values studied in this work are listed in Table A-1. Table 3.5 shows that enthalpy of formation for each molecule: CH_2ClOOH, $CHCl_2OOH$, CCl_3OOH at the CBSQ//B3** calculation level throughout all five reaction schemes is near constant. At the CBSQ//B3** calculation level, $\Delta H_f^\circ{}_{298}$ averaged over five reactions for CH_2ClOOH is -41.78 ± 0.71 kcal/mol; $\Delta H_f^\circ{}_{298}$ for $CHCl_2OOH$ is -45.90 ± 2.00 kcal/mol; $\Delta H_f^\circ{}_{298}$ for CCl_3OOH is -47.63 ± 3.42 kcal/mol. These error values only show the

calculated deviations from the five reaction schemes, and do not include the error from uncertainties in standard compound values.

Table 3.4 Reaction Enthalpies at 298K

Reaction Series	B3LYP /6-31G(d,p)	B3LYP /6-311+G(3df,2p)	QCISD(T) /6-31G(d,p)	CBSQ /B3LYP**
1. $CH_2ClOOH + CH_4 \rightarrow CH_3OOH + CH_3Cl$	7.94	7.24	7.54	7.90
$CHCl_2OOH + CH_4 \rightarrow CH_3OOH + CH_2Cl_2$	7.92	6.80	8.53	8.97
$CCl_3OOH + CH_4 \rightarrow CH_3OOH + CHCl_3$	6.33	4.87	8.27	8.41
2. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CH_2Cl$	3.95	3.11	3.12	2.89
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CHCl_2$	2.06	0.86	1.39	0.49
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CCl_3$	0.36	-0.99	0.02	-1.87
5. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_3Cl$	2.75	2.66	1.89	2.28
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_2Cl_2$	2.74	2.23	2.88	3.35
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CHCl_3$	1.15	0.30	2.62	2.80
3. $CH_2ClOOH + H_2 \rightarrow CH_3OOH + HCl$	-11.07	-13.34	-11.76	-10.83
$CHCl_2OOH + 2H_2 \rightarrow CH_3OOH + 2HCl$	-30.86	-34.25	-29.98	-27.13
$CCl_3OOH + 3H_2 \rightarrow CH_3OOH + 3HCl$	-54.83	-58.81	-51.09	-45.11
4. $CH_2ClOOH + H_2O \rightarrow CH_3OOH + HOCl$	44.49	46.84	45.42	49.85
$CHCl_2OOH + 2H_2O \rightarrow CH_3OOH + 2HOCl$	80.25	86.10	84.39	94.23
$CCl_3OOH + 3H_2O \rightarrow CH_3OOH + 3HOCl$	111.84	121.72	120.47	136.92

a. Reaction enthalpies include thermal correction and zero-point energy. Units in kcal/mol. Reaction series 1, 2 and 3 are isodesmic reaction, 4 and 5 are not. No reaction series conserves groups.

The calculation results for the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), and QCISD(T)/6-31G(d,p) calculation levels result in uniform $\Delta H_f^\circ{}_{298}$ values among three isodesmic reaction schemes. The average $\Delta H_f^\circ{}_{298}$ from three isodesmic reaction schemes at B3LYP/6-31G(d,p) level are -41.94, -44.87, -45.12 kcal/mol for CH_2ClOOH, $CHCl_2OOH$, CCl_3OOH respectively. These values are in good agreement (within $\pm$ 0.5 kcal/mol) with the average $\Delta H_f^\circ{}_{298}$ from the higher level CBSQ//B3** calculations (see also Table 3.5). The agreement suggests that the economical calculations at B3LYP/6-

31G(d,p) level, with isodesmic reactions, will be accurate for similar compounds with large numbers of heavy atoms.

Table 3.5 Calculated $\Delta H_f^\circ{}_{298}$ for Chlorinated Methyl Hydroperoxides [a]

Reaction Series	B3LYP /6-31G(d,p)	B3LYP /6-311+G(3df,2p)	QCISD(T) /6-31G(d,p)	CBSQ /B3LYP**	Error limits [c]
1. $CH_2ClOOH + CH_4 \rightarrow CH_3OOH + CH_3Cl$	-41.45	-39.04	-41.05	-41.41	±1.13
$CHCl_2OOH + CH_4 \rightarrow CH_3OOH + CH_2Cl_2$	-44.66	-43.54	-45.27	-45.71	±1.30
$CCl_3OOH + CH_4 \rightarrow CH_3OOH + CHCl_3$	-44.44	-42.98	-46.38	-46.52	±1.32
2. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CH_2Cl$	-42.35	-41.51	-41.52	-41.29	±1.32
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CHCl_2$	-44.71	-43.51	-44.04	-43.14	±1.73
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CCl_3$	-45.93	-44.58	-45.59	-43.70	±1.47
3. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_3Cl$	-42.01	-41.92	-41.15	-41.54	±0.77
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_2Cl_2$	-45.23	-44.72	-45.37	-45.84	±0.94
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CHCl_3$	-45.01	-44.16	-46.48	-46.66	±0.96
4. $CH_2ClOOH + H_2 \rightarrow CH_3OOH + HCl$	-42.79	-40.52	-42.10	-43.03	±0.99
$CHCl_2OOH + 2H_2 \rightarrow CH_3OOH + 2HCl$	-45.06	-41.67	-45.94	-48.79	±1.04
$CCl_3OOH + 3H_2 \rightarrow CH_3OOH + 3HCl$	-43.15	-39.17	-46.89	-52.87	±1.09
5. $CH_2ClOOH + H_2O \rightarrow CH_3OOH + HOCl$	-36.29	-38.64	-37.22	-41.65	±1.54
$CHCl_2OOH + 2H_2O \rightarrow CH_3OOH + 2HOCl$	-32.05	-37.90	-36.19	-46.02	±2.14
$CCl_3OOH + 3H_2O \rightarrow CH_3OOH + 3HOCl$	-23.64	-33.52	-32.27	-48.72	±2.74
Average value and deviation for CH_2ClOOH [b]:	-41.94±0.45	-40.82±1.56	-41.24±0.25	-41.41±0.13	
Average value and deviation for $CHCl_2OOH$ [b]:	-44.87±0.32	-43.92±0.69	-44.89±0.74	-44.90±1.52	
Average value and deviation for CCl_3OOH [b]:	-45.12±0.75	-43.91±0.83	-46.15±0.49	-45.11±1.99	

a. Units in kcal/mol. Units in kcal/mol. Enthalpy values are reported to 2 decimal places for demonstration of differences between calculation levels; our error analysis shows the values are only accurate to one significant decimal place.

b. Average enthalpy of formation and deviations between reaction schemes 1, 2 and 3. Uncertainties of reference compound enthalpy not included.

c. Deviations from the uncertainty in reference compound Enthalpies.

Overall results among the four calculation methods appear quite consistent for the three isodesmic reaction series. There is reasonable consistency across reaction series 4, which is not isodesmic, but uses H_2 and HCl for element balance for CH_2ClOOH and $CHCl_2OOH$; but the CBSQ//B3LYP/6-31G(d,p) and the B3LYP/6-311+G(3d,2p)

calculations on CCl_3OOH in this series (4) show significant deviations from data in the isodesmic reaction schemes. With the exception of CBSQ//B3** values, enthalpies calculated from use of reaction scheme (5) are not consistent with data from the other four reaction schemes. Analysis from this reaction $CHCl_2OOH + 2H_2O \rightarrow CH_3OOH + 2HOCl$, (set 5) results in consistently high values of $\Delta H_f^\circ{}_{298}$ for $CHCl_2OOH$ by the two density functions and the QCISD(T) calculation methods relative to other reaction schemes and CBSQ//B3** calculation results. Deviations for $\Delta H_f^\circ{}_{298}$ across reaction set (5) appear to scale linearly with the coefficient of H_2O and HOCl, suggesting a significant error in calculation of one or both of these species. The CBSQ//B3** values on the three chloromethyl hydroperoxides show good agreement in this reaction series (5) with data in all calculation methods for the other reaction sets. The tri-chloro value is ca 2 kcal/mol low; but this may result from error in the literature value of HOCl.[50] This provides strong support for accuracy of CBSQ/B3** calculation enthalpies using the methods in this study.

There are three conformers of chloro-methylhydroperoxide and dichloro-methylhydroperoxide respectively. The total electronic energies including ZPVE, thermal correction to 298 K of the conformers in CH_2ClOOH, $CHCl_2OOH$ listed in Table A-3 are estimated at the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculation levels. $\Delta H_f^\circ{}_{298}$ of the rotational conformers are calculated at CBSQ//B3LYP** level using three isodesmic reaction schemes. The statistical distribution and overall $\Delta H_f^\circ{}_{298}$ of three chlorinated methyl hydroperoxides are also listed in Table A-3. Energy difference values of the conformers at the B3LYP/6-311+G(3df,2p), QCISD(T) and CBSQ//B3** levels show similar values.

The energy difference values at CBSQ//B3** calculation level is taken to calculate the statistical distribution of rotation conformers.

The accuracy of the enthalpies of formation obtained theoretically is controlled by several factors: the level of sophistication (method plus basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and the choice of the working chemical reaction used in the cancellation of calculation errors. The maximum uncertainty in enthalpy values for the reference compounds is listed in Table 3.5 (individual compound uncertainties see Table A-1). We note, however, the averaged deviations in enthalpies from the all calculation levels and the isodesmic reaction schemes are within the error limits of CBSQ//B3** values, as are the uncertainty in enthalpy on standards in the work reactions. The ZPVE and thermal correction in data of Table A-1 have small contributions to the error on relative base. Scott and Radom report reaction schemes errors after scaling (0.9806) for B3LYP/6-31G(d,p) of 0.1 kcal/mol for ZPVE in their study on 39 molecules incorporating 1066 known vibrations. They also report reaction schemes error of ca. 0.01 kacl/mol for thermal correction from 0 to 298 K in density function theory.[21] We assume these errors in our calculation to be non ramdom and are cancelled in the isodesmic reactions to a significant extent. The overall average (using the three isodesmic reactions based on all the four calculation level) $\Delta H_f^\circ{}_{298}$ of CH_2ClOOH, $CHCl_2OOH$, CCl_3OOH are -41.34 ± 2.13 kcal/mol, -44.44 ± 2.61 kcal/mol, -45.18 ± 2.69 kcal/mol respectively. The $\Delta H_f^\circ{}_{298}$ from the CBSQ//B3** calculation level (using the three isodesmic reactions) for CH_2ClOOH, $CHCl_2OOH$, CCl_3OOH are -41.40±1.45 kcal/mol, -44.71±3.25 kcal/mol, -45.11±3.46 kcal/mol respectively. Error

limits of $\Delta H_f^\circ{}_{298}$ of three chlorinated methyl hydroperoxides are obtained by adding the errors inherent in the present computational approach and the uncertainties in the experimental heats of formation.

A comparison of enthalpies of formation calculated using density functional and ab initio theory with the semipirical MO methods, AM1 and PM3, is also performed. The results listed in Table B-2 indicate that the PM3 method with isodesmic reaction schemes appears to be a preferred alternative for the calculation of enthalpies of formation for the three chlorinated methyl hydroperoxides among these two semiempirical methods.

3.4.3 Rotational Barriers

Potential barriers for internal rotations of CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH are calculated at the B3LYP/6-31G(d,p) level. Potential energy as function of dihedral angle is determined by scanning the torsion angle of Cl-C-O-H and C-O-O-H from 0° to 360° at 15° intervals and allowing the remaining molecular structural parameters to be optimized. The C-O and O-O torsion in the three chlorinated methyl hydroperoxides have potential consisting of three minima and three maxima. The geometries at the points of these minimum and maximum are fully optimized. The geometries are calculated for all rotational conformers at B3LYP/6-31G(d,p) level. The barriers for internal rotations are calculated from the differences between the total energy of each conformer and that of the global equilibrium. The total energies and calculated rotation barriers about C-O and O-O bonds for each rotational conformer of three chlorinated methyl hydroperoxides are listed in Table C-2 and C-3. Potential energy vs. torsion angle diagrams for internal

rotations about C-O and O-O bond of the three chlorinated methyl hydroperoxides are shown in Figures 3.2, 3.3, 3.4 and 3.5. Points are calculated values at B3LYP/6-31G(d,p) level. Lines are results of the Fourier expansion. The values of the coefficients of the Fourier expansion, a_i and b_i in equation are listed in Table 3.6.

Table 3.6 Coefficients of Truncated Fourier Series Representation Expansions for Internal Rotation Potentials [a]

species	a_0	a_1	a_2	a_3	a_4	a_5
CH_2Cl-OOH	5.031	0.954	4.143	2.290	-0.200	-0.006
$CHCl_2$-OOH	4.173	-0.220	1.786	2.603	-0.130	0.056
CCl_3-OOH	3.513	-0.016	0.169	3.431	-0.177	-0.021
CH_2ClO-OH	3.048	2.384	1.567	0.328	0.080	0.018
$CHCl_2O$-OH	3.317	2.747	1.890	0.300	0.069	0.013
CCl_3O-OH	1.717	1.491	1.793	0.347	0.111	0.025
		b_1	b_2	b_3	b_4	b_5
CH_2Cl-OOH		-0.165	-0.174	-0.560	-0.072	-0.128
$CHCl_2$-OOH		-1.288	2.110	-0.057	0.126	0.025
CCl_3-OOH		0.008	0.053	0.303	0.024	0.002
CH_2ClO-OH		1.577	0.457	0.024	-0.021	-0.015
$CHCl_2O$-OH		1.504	0.542	0.035	-0.025	-0.012
CCl_3O-OH		0.000	0.000	0.000	0.000	0.000

a. Units in kcal/mol. Values of rotation barriers calculated at B3LYP/6-31G(d,p) level are used to calculate the coefficients.

Figure 3.2 shows the calculated rotational barriers about the C-O bond for chloromethylhydroperoxide. The OH-H anti conformer is the most stable conformer because of the least interaction between the two non-bonding electron pair from the O atom and the Cl atom. The OH-Cl eclipsed conformer has the highest rotational barrier, 12.22 kcal/mol. The OH-Cl anti conformer, which has rotational barrier of 5.77 kcal/mol, is more stable than the other two maxima (corresponding to a non-symmetric configuration with O-O bond positioned between the two C-H bonds). This indicates that the former has less electronic interaction between the two non-bonding electron pair from the O atom and the Cl atom than the latter.

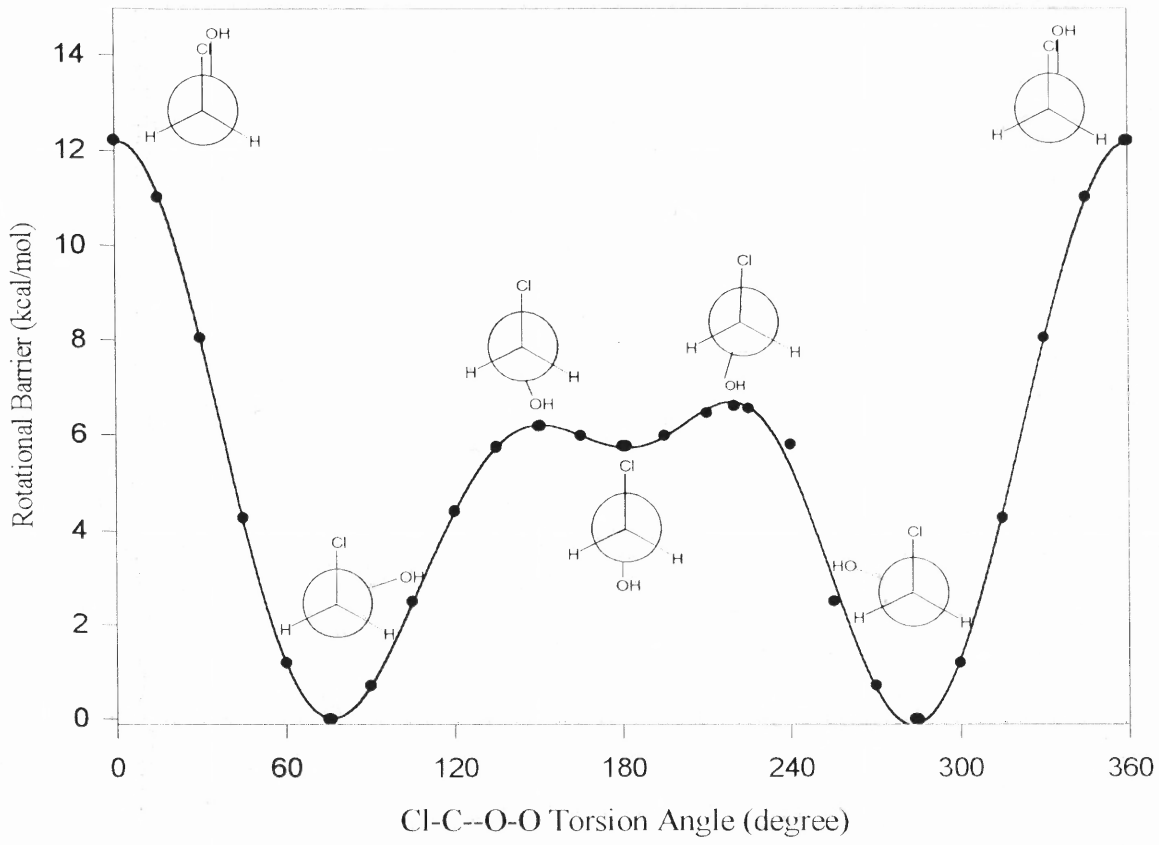


Figure 3.2 Potential barriers for internal rotation about the C-O bond of CH_2ClOOH. Points are calculated values at B3LYP/6-31G(d,p) level of theory. Line is Fourier expansion, with the coefficients listed in Table 3.6. The geometries at the points of minimum and maximum are fully optimized except the points of C-O--O-H dihedral angles at 0° and 150°, at which C-O--O-H dihedral angles are frozen.

Figure 3.3 shows calculated rotational barriers about the C-O bond for dichloromethylhydroperoxide. One of the OH-Cl eclipsed conformers has a slightly higher rotational barrier, 9.48 kcal/mol, than that of the other which has a rotational barrier 8.34 kcal/mol. This is because the H atom in the OH bond is closer to the H atom in the C-H bond in the former conformation. The third maxima corresponding to the OH-H eclipsed conformer is significantly lower (3.30 kcal/mol) due to intramolecular attraction between the H atom in the C-H bond and the O atom in O-H bond. Of the three

minima, rotational barriers of the OH-H anti conformer is 0.35 kcal/mol lower than that of a nonsymmetric OH-Cl anti conformer due to the H atom in the O-H bond which is closer to the Cl atom in the C-Cl bond in this conformer. The third minima, which has a rotational barrier of 2.41 kcal/mol, corresponds to a nonsymmetric configuration with the O-O bond positioned between the C-H and the C-Cl bonds. Its rotational barrier is 2.06 kcal/mol higher than that of the second mimina due to the H atom in the O-H bond which is closer to the H atom in the C-H bond in this conformer.

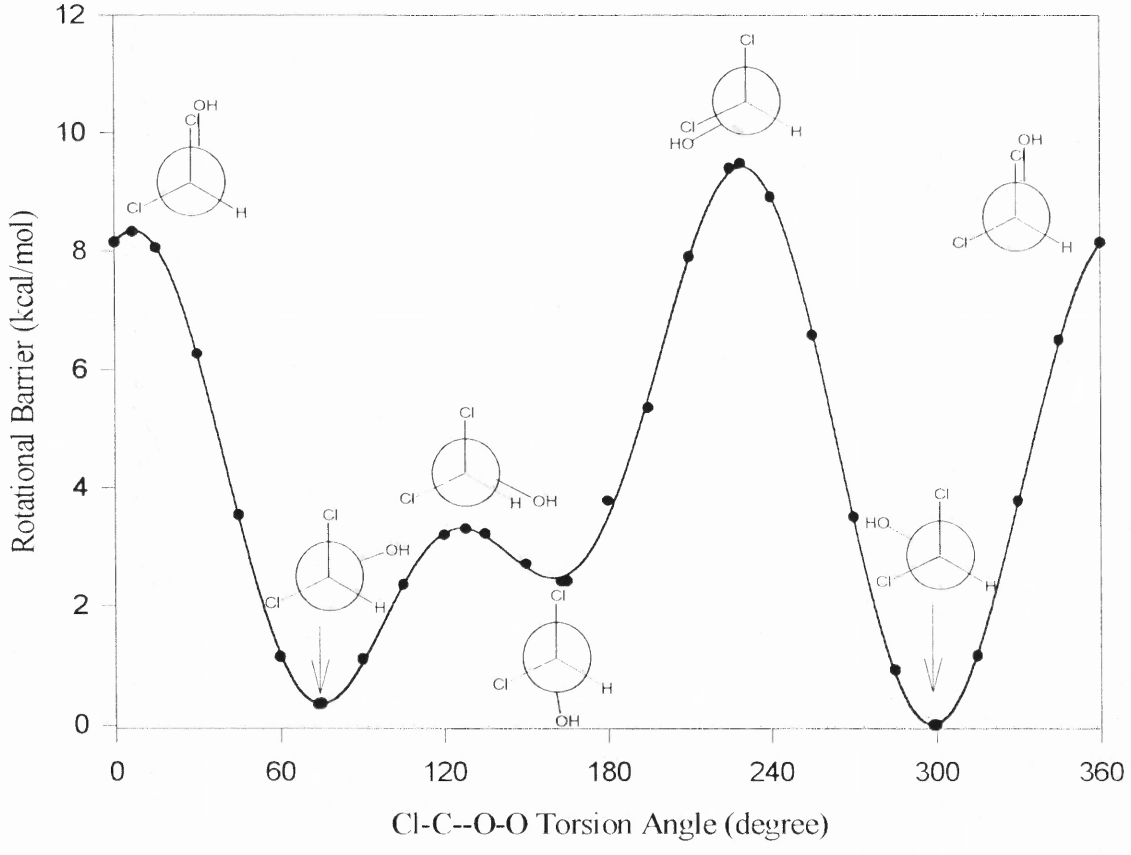


Figure 3.3 Potential barriers for internal rotation about the C-O bond of $CHCl_2OOH$. Points are calculated values at B3LYP/6-31G(d,p) level of theory. Line is Fourier expansion, with the coefficients listed in Table 3.6. The geometries at the points of minimum and maximum potential barriers are fully optimized.

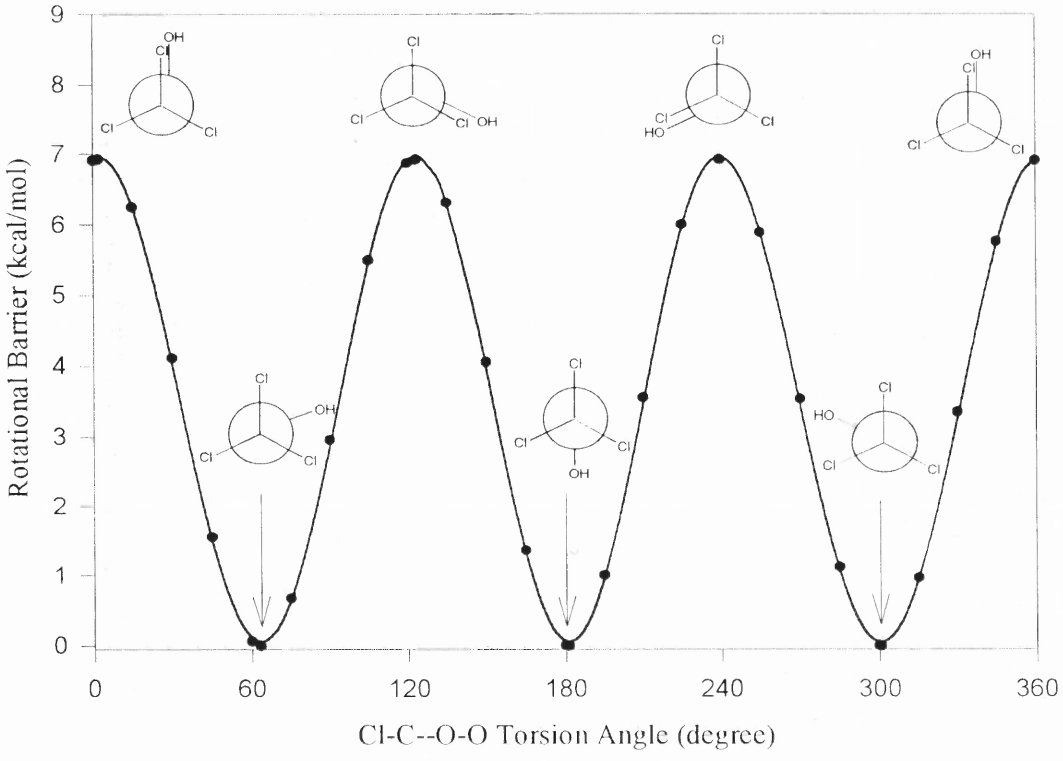


Figure 3.4 Potential barriers for internal rotation about the C-O bond of CCl_3OOH. Points are calculated values at B3LYP/6-31G(d,p) level of theory. Line is Fourier expansions, with the coefficients listed in Table 3.6. The geometries at the points of minimum and maximum are fully optimized except C-O--O-H dihedral angles are frozen at the three maximum.

Figure 3.4 shows the calculated symmetric rotational barriers about the C-O bond for trichloromethylhydroperoxide. The calculation shows that the OH-Cl eclipsed conformer has a rotational barrier of 6.92 kcal/mol above the OH-Cl gauche staggered conformer, which is the most stable conformer.

Figure 3.5 shows calculated rotational barriers about the O-O bond of the three chlorinated methyl hydroperoxides. The rotational barriers about the O-O bond of dichloro-methyl-hydroperoxide is 0.92 kcal/mol higher than that of chloro-methyl-hydroperoxide. Three chlorine atoms on the methyl make the rotation about the C-O

bond symmetric, and the H atom on the hydroxyl makes the rotation about O-O bond symmetric. This is probably the reason why this molecule has the lowest barriers about the C-OO and CO-O torsion among the three chlorinated methyl hydroperoxides.

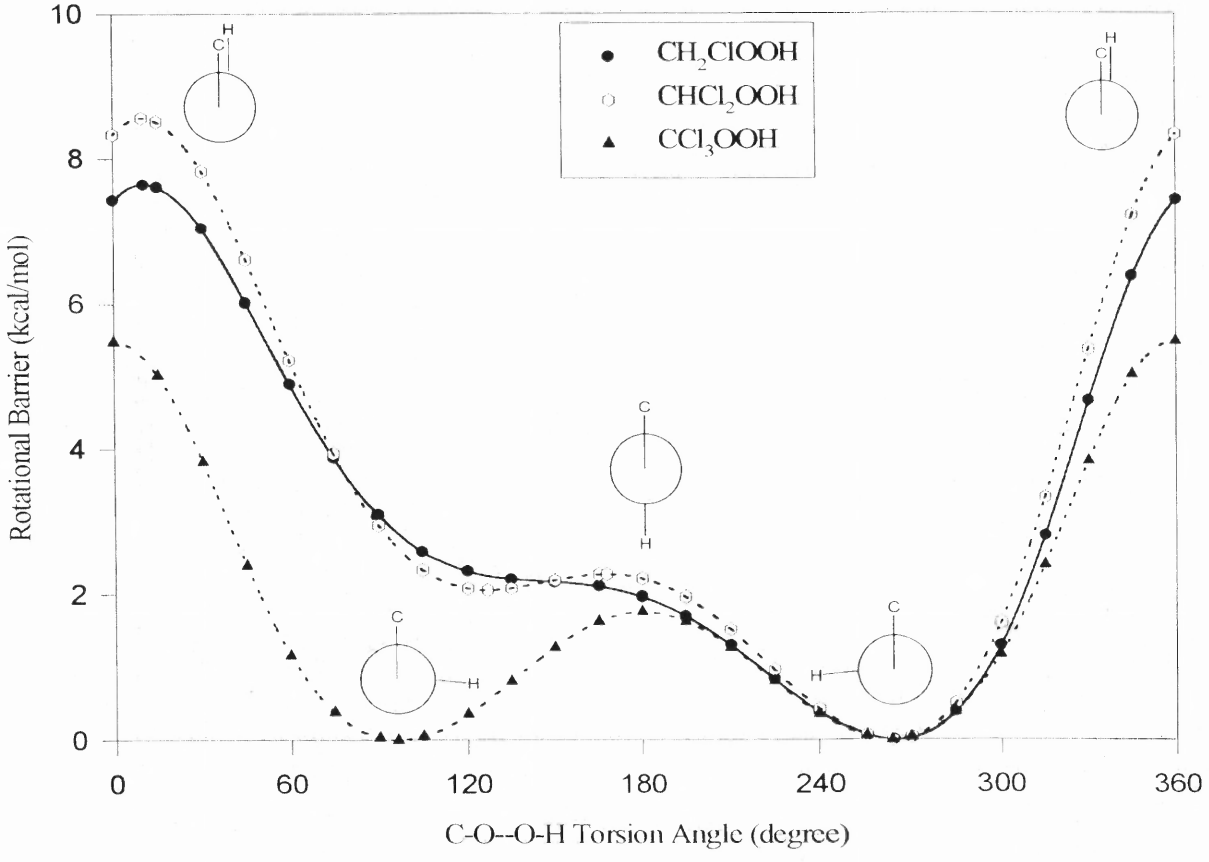


Figure 3.5 Potential barriers for internal rotation about the O-O bond of the three chlorinated methyl hydroperoxides. Points are calculated values at B3LYP/6-31G(d,p) level of theory. Lines are Fourier expansions, with the coefficients listed in Table 3.6. The geometries at the points of minimum and maximum potential barriers are fully optimized.

3.4.4 Entropy (S^{o}_{298}) and Heat Capacity ($C_p(T)$'s ($300 \leq T/K \leq 1500$))

S^{o}_{298} and $C_p(T)$'s calculation results using B3LYP/6-31G(d,p) determined geometries and frequencies are summarized in Table C-2. TVR, represents the sum of the contributions

from translations, external rotations and vibrations for S°_{298} and $C_p(T)$'s. The torsion frequencies calculated for the internal rotors are not included in TVR. Instead, a more exact contribution from hindered rotations is calculated. I.R., represents the contributions from internal rotation about C-O and O-O bonds for S°_{298} and $C_p(T)$'s. Final standard entropies also include correction from rotational conformers. This correction is calculated by the following formula for 1 mole of mixture[35]:

$$\Delta S_{mixing} = -R \sum n_i \ln (n_i) \qquad (2.2)$$

where n_i is the equilibrium mole fraction of the *i*th form. ΔS_{mixing} represents the entropy of mixing of rotational conformations or optical conformations.

Table C-2 also lists comparisons with previous calculation data. The calculation results show the presented values to be about 4.8 kcal/mol lower than the enthalpy data reported by Knyazev et al.[48] We explain this discrepancy as a combination of two effects: one is a slightly stronger peroxy hydrogen bond energy, and the other is occurrence of hydrogen bonding between the peroxy hydrogen atom and a chlorine atom on the methyl group.

3.4.5 Group Additivity Values

The group additivity method,[35] is straightforward and reasonably accurate calculation method to estimate thermodynamic properties of hydrocarbons and oxygenated hydrocarbons,[36] modifications have also been reported that make it useful for chlorinated and fluorinated hydrocarbons.[29,30,37,38] In this work, we develop a set of chloro-oxy hydrocarbon groups derived from the thermodynamic property data of chlorinated methyl hydroperoxides. Values are reported for the groups $C/Cl/H_2/OO$, $C/Cl_2/H/OO$, $C/Cl_3/OO$

derived from CH_2ClOOH, $CHCl_2OOH$, and CCl_3OOH respectively. $\Delta H_f^\circ{}_{298}$ and C_P's of $C/Cl/H_2/O$ are calculated on the basis of

$$(CH_2ClOOH) = (C/Cl/H_2/OO) + (OO/C/H)$$

$S^\circ{}_{298}$ of $C/Cl/H_2/O$ is calculated on the basis of

$$(CH_2ClOOH) = (C/Cl/H_2/OO) + (OO/C/H) + R\ln(\sigma) + OI$$

where R = 1.987 cal/mol K, σ is symmetry number, and OI stands for optical isomer group. The group values of $C/Cl_2/H/OO$, $C/Cl_3/OO$ are estimated in the same manner. Selection of the initial group values is critical to development of group additivity for accurate property estimation, these criteria are fully discussed in reference 36 and 37. The group values for $\Delta H_f^\circ{}_{298}$, $S^\circ{}_{298}$, and C_p (T) of OO/C/H are taken from the existing literature value.[51] The carbon-chlorine-oxygen group values are derived in this work are listed in Table 3.7. Table 3.7 shows that group value for heat of formation decrease with increased number of chlorine atoms but not in a linear progression. The carbon-chlorine-oxygen group value for entropies and heat capacities below 1500 K increase with increased number of chlorine atoms as expected for the increased mass and lower vibrational frequencies.

Table 3.7 Group Values

Groups	$\Delta H_f^\circ{}_{298}$[a]	$S^\circ{}_{298}$[b]	Cp300[b]	Cp400	Cp500	Cp600	Cp800	Cp1000
OO/C/H[c]	-23.50	36.84	9.74	10.47	11.00	11.74	12.19	12.91
$C/Cl/H_2/OO$	-17.90	38.18	8.23	10.43	12.32	13.52	15.79	16.83
$C/Cl_2/H/OO$	-21.21	44.94	12.48	14.67	16.11	16.73	18.07	18.49
$C/Cl_3/OO$	-21.61	50.87	15.15	17.28	18.68	19.25	20.33	20.36

a. Units in kcal/mol.
b. Units in cal/mol-K.
c. Reference 44.

3.5 Summary

Thermodynamic properties of three chlorinated methyl hydroperoxides are calculated using density functional and ab initio method with five reaction schemes for cancellation of errors in energy. Standard enthalpy of formation, $\Delta H_f^\circ{}_{298}$ is calculated using only isodesmic reaction schemes based on B3LYP/6-31G(d, p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculations levels and includes the statistical distribution of rotational conformers. CBSQ//B3** calculation values of $\Delta H_f^\circ{}_{298}$ do not show the large deviations for non isodesmic reactions, that are observed in the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) calculations. Entropies $S^\circ{}_{298}$ and heat capacities ($C_p(T)$'s ($300 \leq T/K \leq 1500$)) are determined by B3LYP/6-31G(d,p) optimized geometries and frequencies, and entropy correction for mixing of rotational conformers are included. Enthalpy, entropy and $C_p(T)$ properties are determined for C/Cl/H_2/OO, C/Cl_2/H/OO, and C/Cl_3/OO chloro-peroxy group for use in group additivity. Intramolecular torsion potentials are also determined.

CHAPTER 4

CONCLUSION

Thermodynamic Properties of chloro-methanol, di-chloro-methanol, tri-chloro-methanol, chloro-methyl-hydroperoxide, di-chloro-methyl-hydroperoxide, and tri-chloro-methyl-hydroperoxide are calculated using density functional and ab initio methods with five reaction schemes for cancellation of errors in energy. Standard enthalpy of formation, $\Delta H_f^\circ{}_{298}$ is calculated using only isodesmic reaction schemes based on B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) and CBSQ//B3LYP/6-31G(d,p) calculations levels and includes the statistical distribution of rotational conformers. CBSQ//B3LYP/6-31G(d,p) calculation values of $\Delta H_f^\circ{}_{298}$ do not show the large deviations for non-isodesmic reactions, that are observed in the B3LYP/6-31G(d,p), B3LYP/6-311+G(3df,2p), QCISD(T)/6-31G(d,p) calculations. Entropies $S^\circ{}_{298}$ and heat capacities ($C_p(T)$'s ($300 \leq T/K \leq 1500$)) are determined by B3LYP/6-31G(d,p) optimized geometries and frequencies, and entropy correction for mixing of rotational conformers are included. Evaluation of data from the reactions, results in $\Delta H_f^\circ{}_{298}$ values for CH_2ClOH of -58.0±0.5 kcal/mol, $CHCl_2OH$ of -64.4±2 kcal/mol and CCl_3OH of -65.0±2 kcal/mol, CH_2ClOOH of -41.4±1kcal/mol, $CHCl_2OOH$ of -44.7±3 kcal/mol and CCl_3OOH of -45.1±3 kcal/mol. Enthalpy, entropy and $C_p(T)$ properties are determined for $C/Cl/H_2/O$, $C/Cl_2/H/O$, $C/Cl_3/O$, $C/Cl/H_2/OO$, $C/Cl_2/H/OO$, and $C/Cl_3/OO$ chloro-peroxy group for use in group additivity. Enthalpy values for the $C/Cl/H_2/O$, $C/Cl_2/H/O$ and $C/Cl_3/O$ groups are -20.1, -26.5, and -27.1 kcal/mol respectively. Enthalpy values for the $C/Cl/H_2/OO$, $C/Cl_2/H/OO$ and $C/Cl_3/OO$ groups are -17.9, -21.2, and -21.6 kcal/mol

respectively. Error limits are the same as that of corresponding molecule. Enthalpy values from the isodesmic reaction show good agreement at all theory level, suggesting effective cancellation of errors in these reaction sets. CBSQ//B3LYP/6-31G(d,p) calculations are judged to be the most accurate in this study, especially for non-isodesmic reaction systems.

APPENDIX A

TOTAL ENERGIES AT 298 K AND $\Delta H_f^\circ{}_{298}$ FOR SPECIES AND RELATED ROTATIONAL CONFORMERS IN REACTION SCHEMES

This appendix contains following tables:

A-1 Total energies at 298 K and $\Delta H_f^\circ{}_{298}$ for species in reaction schemes.

A-2 Total energy, $\Delta H_f^\circ{}_{298}$ and barriers of H-H and H-Cl anti conformer in $CHCl_2OH$.

A-3 Total energy of the conformers, relative fraction, and overall $\Delta H_f^\circ{}_{298}$ for chlorinated methyl hydroperoxides.

Table A-1 Total Energies [a] at 298 K and $\Delta H_f^\circ{}_{298}$ for Species in Reaction Schemes

	B3LYP /6-31G(d,p)	B3LYP /6-311+G(3df,2p)	QCISD(T) /6-31G(d,p)	CBSQ//B3LYP /6-31G(d,p)	ZPVE[b]	Therm. Corr.[c]	$\Delta H_f^\circ{}_{298}$ [d]
CH_2ClOH	-575.2793126	-575.3604144	-574.4029547	-574.6988236	26.74	2.91	
$CHCl_2OH$	-1034.8805222	-1034.9952721	-1033.4425547	-1033.8597902	20.96	3.40	
CCl_3OH	-1494.4680253	-1494.6179333	-1492.4711754	-1493.0111533	14.34	4.12	
CH_2ClOOH	-650.4053531	-650.5138133	-649.3499702	-649.7512186	28.66	3.60	
$CHCl_2OOH$	-1109.9994246	-1110.1422329	-1108.3836359	-1108.9064954	22.68	4.19	
CCl_3OOH	-1569.5868417	-1569.7648282	-1567.4126991	-1568.0590909	16.23	4.90	
CH_4	-40.4760617	-40.4887941	-40.3416050	-40.4053008	27.70	2.39	-17.89 ±0.07
CH_3Cl	-500.0713970	-500.1177433	-499.3735466	-499.5567138	23.33	2.49	-19.60 ±0.12
CH_2Cl_2	-959.6654913	-959.7468506	-958.4056312	-958.7102821	18.13	2.84	-22.83 ±0.29
$CHCl_3$	-1419.2554379	-1419.3725278	-1417.4351135	-1417.8637645	12.23	3.40	-24.20 ±0.31
CH_3OH	-115.6693145	-115.7182535	-115.3577315	-115.5342419	31.63	2.67	-48.08 ±0.05
H_2O	-76.3950062	-76.4385182	-76.2069081	-76.3329532	13.15	2.37	-57.80 ± 0.1
HOCl	-535.9320865	-536.0043607	-535.1784778	-535.4175126	8.07	2.44	-17.80 ± 0.5
H_2	-1.1652606	-1.1667351	-1.1518653	-1.1625320	6.26	2.07	0.00 ± 0.0
HCl	-460.7908786	-460.8284749	-460.2145668	-460.3437852	4.14	2.07	-22.06 ±0.05
CH_3CH_3	-79.7608472	-79.7836024	-79.5076398	-79.6247781	46.10	2.77	-20.24 ±0.12
CH_3CH_2Cl	-539.3625421	-539.4191202	-538.5466250	-538.7841686	41.12	3.12	-26.84±0.26
CH_3CHCl_2	-998.9596199	-999.0511320	-997.5830538	-997.9432661	35.45	3.63	-31.09 ±0.67
CH_3CCl_3	-1458.5497382	-1458.6766779	-1456.6142988	-1457.0996327	29.21	4.28	-34.01 ±0.41
CH_3CH_2OH	-154.9628217	-155.0210006	-154.5326366	-154.7628412	49.37	3.25	-56.12 ± 0.2
CH_3OOH	-190.7973701	-190.8733326	-190.3060132	-190.5872201	33.68	3.30	-31.8 ±0.94
CH_3CH_2OOH	-230.0904144	-230.1754257	-229.4810497	-229.8159655	51.37	3.96	-39.9 ±0.53

a. Total energy calculation based on the geometries optimized at B3LYP/6-31G(d,p) level of theory and ZPVE's and thermal corrections to 298 K are included. Units in Hartree.
b. ZPVE: scaled zero-point energies in kcal/mol. ZPVE is scaled by 0.9806 (Scott and Radom).
c. Therm.Corr.: Thermal corrections in kcal/mol.
d. Units in kcal/mol. The uncertainties are evaluated from reference 39 and 40.

Table **A-2 Total Energy, $\Delta H_f^\circ{}_{298}$ and Barriers of H-H and H-Cl anti Conformer in $CHCl_2OH$**

	B3LYP /6-31G(d,p)	B3LYP /6-311+G(3df,2p)	QCISD(T) /6-31G(d,p)	CBSQ//B3LYP /6-31G(d,p)	Average $\Delta H_f^\circ{}_{298}$
$CHCl_2OH(1)$[a] (hartree)	-1034.8805222	-1034.9952721	-1033.4425547	-1033.8597902	
$CHCl_2OH(2)$[b] (hartree)	-1034.8746852	-1034.9905220	-1033.4376007	-1033.8551027	
$\Delta H_f^\circ{}_{298}$[c] (kcal/mol)	-63.11±0.95	-62.16±1.26	-62.59±1.59	-62.12±2.31	-62.50±1.68[e]
Barrier[d] (kcal/mol)	3.66	2.98	3.11	2.94	3.01[f]

a. Total electronic energies including ZPVE and thermal correction to 298K of the H-H anti conformer in$CHCl_2OH$.
a. Total electronic energies including ZPVE and thermal correction to 298K of the H-Cl anti conformer in $CHCl_2OH$.
b. Enthalpy of formation at 298 K of the H-Cl anti conformer in $CHCl_2OH$ calculated by three isodesmic reaction schemes.
c. Total electronic energy difference between H-Cl anti conformer and the H-H anti conformer in $CHCl_2OH$.
d. Average $\Delta H_f^\circ{}_{298}$ of H-Cl anti conformer at all the four calculation levels using three isodesmic reaction schemes.
e. Average value of the calculation at the B3LYP/6-311+G(3df,2p), QCISD(T) and CBSQ//B3** levels.

Table A-3 Total Energy of the Conformers, Relative Fraction, and Overall $\Delta H_f{}^\circ_{298}$ for Chlorinated Methyl Hydroperoxides

	B3LYP /6-31G(d,p)	B3LYP /6-311+G(3df,2p)	QCISD(T) /6-31G(d,p)	CBSQ//B3LYP /6-31G(d,p)	$\Delta H_f{}^\circ_{298}$ [g] CBSQ	Relative fraction	Final $\Delta H_f{}^\circ_{298}$
$CH_2ClOOH(2)$[a]	-650.4053531	-650.5138133	-649.3499702	-649.7512186	-41.41	0.49936	
$CH_2ClOOH(1)$[b]	-650.3963480	-650.5059732	-649.3430880	-649.7442712	-36.99	0.00128	-41.40±1.45
Δ Energy [d]	5.65	4.92	4.32	4.36			
$CHCl_2OOH(1)$[a]	-1109.9994246	-1110.1422329	-1108.3836359	-1108.9064954	-44.90	0.60149	
$CHCl_2OOH(1)$[b]	-1109.9956912	-1110.1391998	-1108.3808470	-1108.9036484	-44.54	0.36866	
$CHCl_2OOH(1)$[c]	-1109.9989063	-1110.1419820	-1108.3836551	-1108.9060332	-43.05	0.02985	-44.71±3.25
Δ Energy [e]	0.33	0.16	-0.01	0.29			
Δ Energy [f]	2.34	1.90	1.75	1.79			
CCl_3OOH	-1569.5868417	-1569.7648282	-1567.4126991	-1569.5868417	-45.11	1.0000	-45.11±3.46

a. Total electronic energies including ZPVE and thermal correction to 298K of the OH-H anti conformer in CH_2ClOOH and $CHCl_2OOH$. Units in hartree.
b. Total electronic energies including ZPVE and thermal correction to 298K of the OH-Cl anti conformer in CH_2ClOOH and $CHCl_2OOH$. Units in hartree.
c. Total electronic energies including ZPVE and thermal correction to 298K of the OH-Cl anti conformer in $CHCl_2OOH$. Units in hartree.
d. Total electronic energy difference between OH-Cl anti conformer and the OH-H anti conformer in CH_2ClOOH. Units in kcal/mol.
e. Total electronic energy difference between OH-Cl anti conformer which has lower energy and the OH-H anti conformer in $CHCl_2OOH$. Units in kcal/mol.
f. Total electronic energy difference between OH-Cl anti conformer which has higher energy and the OH-H anti conformer in $CHCl_2OOH$. Units in kcal/mol.
g. Enthalpy of formation at 298 K calculated at CBSQ//B3LYP/6-31G(d,p) level.

APPENDIX B

REACTION ENTHALPIES AND ENTHALPIES OF FORMATION CALCULATION USING SEMI-EMPIRICAL AM1 AND PM3 METHODS

This appendix contains following tables:

B-1 Reaction enthalpies and $H_f^{\circ}{}_{298}$ for chlorinated methanols using semi-empirical AM1 and PM3 methods.

B-2 Reaction enthalpies and enthalpies of formation for chlorinated methyl hydroperoxides using semi-empirical AM1 and PM3 methods.

Table B-1 Reaction Enthalpies and $H_f^\circ{}_{298}$ for Chlorinated Methanols Using Semi-Empirical AM1 and PM3 Methods

Reaction Series	$\Delta H_{rxn,\,298}$[a]		$\Delta H_f^\circ{}_{298}$[b]	
	AM1	PM3	AM1	PM3
1. $CH_2ClOH + CH_4 \rightarrow CH_3OH + CH_3Cl$	-1.586	5.109	-48.20	-54.90
$CHCl_2OH + CH_4 \rightarrow CH_3OH + CH_2Cl_2$	-4.627	9.211	-48.39	-62.23
$CCl_3OH + CH_4 \rightarrow CH_3OH + CHCl_3$	-12.035	9.439	-42.36	-63.83
2. $CH_2ClOH + CH_3CH_3 \rightarrow CH_3OH + CH_3CH_2Cl$	-0.166	2.847	-54.51	-57.53
$CHCl_2OH + CH_3CH_3 \rightarrow CH_3OH + CH_3CHCl_2$	-1.248	4.944	-57.68	-63.87
$CCl_3OH + CH_3CH_3 \rightarrow CH_3OH + CH_3CCl_3$	-6.329	3.520	-55.52	-65.37
3. $CH_2ClOH + CH_3CH_3 \rightarrow CH_3CH_2OH + CH_3Cl$	-0.149	3.383	-55.33	-58.86
$CHCl_2OH + CH_3CH_3 \rightarrow CH_3CH_2OH + CH_2Cl_2$	-3.190	7.485	-55.52	-66.20
$CCl_3OH + CH_3CH_3 \rightarrow CH_3CH_2OH + CHCl_3$	-6.336	7.713	-53.74	-67.79
4. $CH_2ClOH + H_2 \rightarrow CH_3OH + HCl$	-10.842	-0.225	-59.30	-69.92
$CHCl_2OH + 2H_2 \rightarrow CH_3OH + 2HCl$	-26.409	-0.658	-65.80	-91.55
$CCl_3OH + 3H_2 \rightarrow CH_3OH + 3HCl$	-50.098	-3.696	-64.17	-110.57
5. $CH_2ClOH + H_2O \rightarrow CH_3OH + HOCl$	46.066	25.909	-54.15	-33.99
$CHCl_2OH + 2H_2O \rightarrow CH_3OH + 2HOCl$	87.407	51.610	-55.49	-19.69
$CCl_3OH + 3H_2O \rightarrow CH_3OH + 3HOCl$	120.626	74.706	-48.71	-2.79
$\Delta H_f^\circ{}_{298}$ of CH_2ClOH[c]:			-65.602	-58.650
$\Delta H_f^\circ{}_{298}$ of $CHCl_2OH$[c]:			-69.462	-65.215
$\Delta H_f^\circ{}_{298}$ of CCl_3OH[c]:			-65.200	-69.175

a. Reaction enthalpies at 298 K calculated by five reaction schemes. Units in kcal/mol.
b. Enthalpies of formation at 298 K calculated by five reaction schemes. Units in kcal/mol.
c. Enthalpies of formation at 298 K calculated by MOPAC program directly.

Table B-2 Reaction Enthalpies and Enthalpies of Formation for Chlorinated Methyl Hydroperoxides Using Semi-Empirical AM1 and PM3 Methods

Reaction Series	$\Delta H_{rxn,\ 298}$ [a]		$\Delta H_{f\ 298}^{\circ}$ [b]	
	AM1	PM3	AM1	PM3
1. $CH_2ClOOH + CH_4 \rightarrow CH_3OOH + CH_3Cl$	-2.889	3.084	-30.62	-36.59
$CHCl_2OOH + CH_4 \rightarrow CH_3OOH + CH_2Cl_2$	-9.259	4.747	-27.48	-41.48
$CCl_3OOH + CH_4 \rightarrow CH_3OOH + CHCl_3$	-16.882	3.360	-21.22	-41.47
2. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CH_2Cl$	-1.469	0.822	-36.93	-39.22
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CHCl_2$	-5.880	0.480	-36.81	-43.17
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3OOH + CH_3CCl_3$	-11.176	-2.559	-34.43	-43.05
3. $CH_2ClOOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_3Cl$	-0.828	2.558	-38.47	-41.86
$CHCl_2OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CH_2Cl_2$	-7.198	4.221	-35.33	-46.75
$CCl_3OOH + CH_3CH_3 \rightarrow CH_3CH_2OOH + CHCl_3$	-14.821	2.834	-29.08	-46.73
4. $CH_2ClOOH + H_2 \rightarrow CH_3OOH + HCl$	-12.145	-2.250	-41.72	-51.61
$CHCl_2OOH + 2H_2 \rightarrow CH_3OOH + 2HCl$	-31.041	-5.122	-44.89	-70.80
$CCl_3OOH + 3H_2 \rightarrow CH_3OOH + 3HCl$	-54.945	-9.775	-43.04	-88.21
5. $CH_2ClOOH + H_2O \rightarrow CH_3OOH + HOCl$	44.763	23.884	-36.56	-15.68
$CHCl_2OOH + 2H_2O \rightarrow CH_3OOH + 2HOCl$	82.775	47.146	-34.58	1.05
$CCl_3OOH + 3H_2O \rightarrow CH_3OOH + 3HOCl$	115.779	68.627	-27.58	19.57
$\Delta H_{f\ 298}^{\circ}$ of CH_2ClOOH [c]:			-38.659	-41.890
$\Delta H_{f\ 298}^{\circ}$ of $CHCl_2OOH$ [c]:			-39.190	-46.016
$\Delta H_{f\ 298}^{\circ}$ of CCl_3OOH [c]:			-34.713	-48.361

a. Reaction enthalpies at 298 K calculated by five reaction schemes. Units in kcal/mol.
b. Enthalpies of formation at 298 K calculated by five reaction schemes. Units in kcal/mol.
c. Enthalpies of formation at 298 K calculated by MOPAC program directly.

APPENDIX C

TOTAL ENERGY OF ROTATIONAL CONFORMER AND INTERNAL ROTATION BARRIERS CALCULATION

This appendix contains following tables:

C-1 Total energy, zero point vibrational energies, thermal correction, and internal rotation barriers of chlorinated methanols.

C-2 Total energy and internal rotation barriers about C-O bond of chlorinated methyl hydroperoxides.

C-3 Total energy and internal rotation barriers about O-O bond of chlorinated methyl hydroperoxides.

Table C-1 Total Energy, Zero Point Vibrational Energies, Thermal Correction, and Internal Rotation Barriers of Chlorinated Methanols

Species	Torsion angle	Total Energy[a]	ZPVE [b]	$H_{thermal}$ [c]	Barrier[d]
CH_2Cl-OH	0.0	-575.3206489	26.12	2.72	3.56
	30.0	-575.3231841	26.12	2.72	1.97
	60.0	-575.3263718	26.28	2.68	0.09
	67.8	-575.3265536	26.30	2.68	0.00
	90.0	-575.3252625	26.22	2.73	0.78
	120.0	-575.3210691	26.19	2.72	3.37
	150.0	-575.3180399	26.07	2.70	5.14
	180.0	-575.3173181	25.99	2.70	5.50
	180.1	-575.3173182	25.99	2.70	5.50
	210.0	-575.3180399	26.07	2.70	5.14
	240.0	-575.3210690	26.19	2.72	3.37
	270.0	-575.3252625	26.22	2.73	0.78
	292.2	-575.3265536	26.30	2.68	0.00
	300.0	-575.3263725	26.28	2.68	0.09
	330.0	-575.3231841	26.12	2.72	1.97
	360.0	-575.3206489	26.12	2.72	3.56
$CHCl_2$-OH	0.0	-1034.9128861	20.29	3.22	3.87
	30.0	-1034.9168009	20.33	3.21	1.45
	60.0	-1034.9193425	20.58	3.11	0.00
	61.6	-1034.9193505	20.58	3.11	0.00
	90.0	-1034.9172508	20.39	3.20	1.21
	120.0	-1034.9131777	20.31	3.22	3.70
	141.5	-1034.9121101	20.26	3.21	4.32
	150.0	-1034.9122424	20.25	3.21	4.22
	180.0	-1034.9131149	20.27	3.19	3.68
	182.4	-1034.9131246	20.28	3.19	3.68
	210.0	-1034.9122613	20.31	3.20	4.27
	240.0	-1034.9112459	20.34	3.20	4.94
	240.6	-1034.9112454	20.34	3.20	4.94
	270.0	-1034.9121932	20.30	3.20	4.30
	299.1	-1034.9131244	20.28	3.18	3.68
	300.0	-1034.9131238	20.28	3.19	3.68
	330.0	-1034.9123180	20.25	3.21	4.18
	341.6	-1034.9121101	20.26	3.21	4.32
	360.0	-1034.9128861	20.29	3.22	3.87
CCl_3-OH	0.0	-1494.4944532	13.87	3.88	1.82
	30.0	-1494.4959994	13.87	3.88	0.85
	60.0	-1494.4974472	14.02	3.79	0.00
	90.0	-1494.4960045	13.88	3.88	0.84
	120.0	-1494.4944533	13.87	3.88	1.82
	150.0	-1494.4959668	13.88	3.88	0.87
	180.0	-1494.4974495	14.03	3.79	0.01
	210.0	-1494.4959683	13.88	3.88	0.87
	240.0	-1494.4944536	13.87	3.88	1.82
	270.0	-1494.4960043	13.88	3.88	0.84
	300.0	-1494.4974477	14.02	3.79	0.00
	330.0	-1494.4960000	13.87	3.88	0.85
	360.0	-1494.4944532	13.87	3.88	1.82

a. Total energies at 0 K. Units in hartree.
b. ZPVE with the frequency of the torsion motion about C-O bond excluded.
c. Thermal Correction to 298 K with the frequency of the torsion motion about C-O bond excluded.
d. Rotational barriers are calculated as the difference in total energies + scaled (0.9806) zero-point vibrational energies + thermal correction to 298 K, where the corresponding torsional frequencies are excluded in the calculation of ZPVE and thermal correction. Units in kcal/mol.

Table C-2 Total Energy and Internal Rotation Barriers about C-O Bond of Chlorinated methyl hydroperoxides

CH_2ClOOH			$CHCl_2OOH$			CCl_3OOH		
Torsion angle	Total Energy [a]	Barrier [b]	Torsion angle	Total Energy [a]	Barrier [b]	Torsion angle	Total Energy [a]	Barrier [b]
0.0	-650.4372831	12.22	0.0	-1110.0293039	8.15	0.0	-1569.6094971	6.91
15.0	-650.4391683	11.03	6.7	-1110.0289983	8.34	2.1	-1569.6094689	6.92
30.0	-650.4439082	8.06	15.0	-1110.0294478	8.06	15.0	-1569.6105499	6.24
45.0	-650.4499273	4.28	30.0	-1110.0323102	6.26	30.0	-1569.6139585	4.11
60.0	-650.4548503	1.19	45.0	-1110.0366691	3.53	45.0	-1569.6180278	1.55
75.0	-650.4567427	0.01	60.0	-1110.0404767	1.14	60.0	-1569.6204032	0.06
76.0	-650.4567506	0.00	73.8	-1110.0417347	0.35	63.4	-1569.6205012	0.00
90.0	-650.4556110	0.72	75.0	-1110.0417248	0.35	75.0	-1569.6194281	0.67
105.0	-650.4527657	2.50	90.0	-1110.0405283	1.11	90.0	-1569.6157761	2.97
120.0	-650.4497065	4.42	105.0	-1110.0385394	2.35	105.0	-1569.6117443	5.50
135.0	-650.4475859	5.75	120.0	-1110.0371935	3.20	120.0	-1569.6095559	6.87
150.0	-650.4468907	6.19	128.0	-1110.0370285	3.30	123.4	-1569.6094688	6.92
150.6	-650.4468894	6.19	135.0	-1110.0371600	3.22	135.0	-1569.6104530	6.31
165.0	-650.4472135	5.98	150.0	-1110.0379792	2.71	150.0	-1569.6140504	4.05
180.0	-650.4475576	5.77	162.8	-1110.0384551	2.41	165.0	-1569.6183459	1.35
181.2	-650.4475588	5.77	165.0	-1110.0384390	2.42	180.0	-1569.6204843	0.01
195.0	-650.4472155	5.98	180.0	-1110.0362754	3.77	181.3	-1569.6205012	0.00
210.0	-650.4464680	6.45	195.0	-1110.0337515	5.36	195.0	-1569.6189098	1.00
220.0	-650.4462347	6.60	210.0	-1110.0296895	7.91	210.0	-1569.6148414	3.55
225.0	-650.4463113	6.55	225.0	-1110.0273141	9.40	225.0	-1569.6109433	6.00
240.0	-650.4475002	5.80	229.1	-1110.0271841	9.48	239.5	-1569.6094689	6.92
255.0	-650.4527657	2.50	240.0	-1110.0280798	8.92	240.0	-1569.6094709	6.92
270.0	-650.4556105	0.72	255.0	-1110.0318007	6.58	255.0	-1569.6111263	5.88
283.8	-650.4567510	0.00	270.0	-1110.0367264	3.49	270.0	-1569.6148727	3.53
285.0	-650.4567427	0.01	285.0	-1110.0408235	0.92	285.0	-1569.6187284	1.11
300.0	-650.4548503	1.19	299.0	-1110.0422901	0.00	300.0	-1569.6204958	0.00
315.0	-650.4499273	4.28	300.0	-1110.0422809	0.01	300.7	-1569.6205008	0.00
330.0	-650.4439082	8.06	315.0	-1110.0404365	1.16	315.0	-1569.6189705	0.96
345.0	-650.4391682	11.03	330.0	-1110.0362891	3.77	330.0	-1569.6151547	3.35
359.1	-650.4372764	12.22	345.0	-1110.0319424	6.49	345.0	-1569.6113199	5.76
360.0	-650.4372831	12.22	360.0	-1110.0293039	8.15	360.0	-1569.6094966	6.91

a. Electronic energies at 0K. ZPVE and Thermal correction to 298 K are not included. Units in hartree.

b. Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

Table C-3 Total Energy and Internal Rotation Barriers about O-O Bond of Chlorinated methyl hydroperoxides

CH_2ClOOH			$CHCl_2OOH$			CCl_3OOH		
Torsion angle	Total Energy [a]	barrier [b]	Torsion angle	Total Energy [a]	barrier [b]	Torsion angle	Total Energy [a]	barrier [b]
0.0	-650.4449199	7.42	0.0	-1110.0284528	8.33	0.0	-1569.6117636	5.48
10.6	-650.4445757	7.64	10.0	-1110.0280931	8.56	15.0	-1569.6125053	5.02
15.0	-650.4446333	7.60	15.0	-1110.0281711	8.51	30.0	-1569.6144027	3.83
30.0	-650.4455505	7.03	30.0	-1110.0292655	7.82	45.0	-1569.6166833	2.40
45.0	-650.4471681	6.01	45.0	-1110.0312100	6.60	60.0	-1569.6186244	1.18
60.0	-650.4489575	4.89	60.0	-1110.0334127	5.22	75.0	-1569.6198830	0.39
75.0	-650.4505686	3.88	75.0	-1110.0354500	3.94	90.0	-1569.6204505	0.03
90.0	-650.4518110	3.10	90.0	-1110.0370340	2.95	96.4	-1569.6205011	0.00
105.0	-650.4526270	2.59	105.0	-1110.0380153	2.33	105.0	-1569.6204147	0.05
120.0	-650.4530595	2.32	120.0	-1110.0384198	2.08	120.0	-1569.6199263	0.36
135.0	-650.4532328	2.21	126.9	-1110.0384555	2.06	135.0	-1569.6192023	0.82
150.0	-650.4532936	2.17	135.0	-1110.0384172	2.08	150.0	-1569.6184577	1.28
165.0	-650.4533859	2.11	150.0	-1110.0382423	2.19	165.0	-1569.6179011	1.63
180.0	-650.4536172	1.97	165.0	-1110.0381112	2.27	180.0	-1569.6176958	1.76
195.0	-650.4540429	1.70	167.8	-1110.0381070	2.28	180.1	-1569.6176958	1.76
210.0	-650.4546590	1.31	180.0	-1110.0382019	2.22	195.0	-1569.6179014	1.63
225.0	-650.4553961	0.85	195.0	-1110.0386031	1.97	210.0	-1569.6184577	1.28
240.0	-650.4561356	0.39	210.0	-1110.0393032	1.53	225.0	-1569.6192022	0.82
255.0	-650.4566502	0.06	225.0	-1110.0401827	0.97	240.0	-1569.6199261	0.36
264.3	-650.4567505	0.00	240.0	-1110.0410402	0.44	255.0	-1569.6204148	0.05
270.0	-650.4567084	0.03	255.0	-1110.0416247	0.07	263.7	-1569.6205012	0.00
285.0	-650.4561268	0.39	263.9	-1110.0417349	0.00	270.0	-1569.6204505	0.03
300.0	-650.4546781	1.30	270.0	-1110.0416729	0.04	285.0	-1569.6198828	0.39
315.0	-650.4522834	2.80	285.0	-1110.0409207	0.51	300.0	-1569.6186247	1.18
330.0	-650.4493225	4.66	300.0	-1110.0391665	1.61	315.0	-1569.6166838	2.40
345.0	-650.4466024	6.37	315.0	-1110.0364283	3.33	330.0	-1569.6144028	3.83
360.0	-650.4449199	7.42	330.0	-1110.0331786	5.37	345.0	-1569.6125056	5.02
			345.0	-1110.0302564	7.20	360.0	-1569.6117645	5.48
			360.0	-1110.0284536	8.33	360.0	-1569.6117641	5.48

a. Electronic energies at 0K. ZPVE and Thermal correction to 298 K are not included. Units in hartree.

b. Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

APPENDIX D

IDEAL GAS-PHASE THERMODYNAMIC PROPERTIES CALCULATION

This appendix contains following tables:

D-1 Ideal gas-phase thermodynamic properties of chlorinated methanols.

D-2 Ideal gas-phase thermodynamic properties of chlorinated methyl hydroperoxides.

Table D-1 Ideal Gas-phase Thermodynamic Properties of Chlorinated Methanols [a]

Species and Symmetry No.		$\Delta H_f^\circ{}_{298}$ [b]	$S^\circ{}_{298}$ [c]	Cp300[c]	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
CH_2ClOH	TVR [d]		63.09	11.43	13.65	15.68	17.39	20.03	21.97	25.07
(1)	I.R.[e]		2.53	1.75	2.03	2.16	2.19	2.08	1.91	1.56
	Total [f]	-58.00±0.50	65.62	13.18	15.68	17.84	19.58	22.11	23.88	26.63
	Schneider et al [g]	-58.8								
	Melius [h]	-55.50	71.5	12.45		16.92		21.27	23.26	26.40
	Tyndall [i]	-50.4	63.82							
$CHCl_2OH$	TVR [d]		69.60	14.68	17.13	19.06	20.55	22.68	24.14	26.39
(1)	I.R.[e]		1.24	2.23	3.08	3.49	3.48	2.96	2.41	1.65
	Total [f]	-64.42±2.31	71.10	16.91	20.21	22.55	24.03	25.64	26.55	28.04
	Schneider et al [g]	-66.3								
	Melius [h]	-66.40	72.5	16.50		20.60		24.02	25.40	27.64
	Tyndall [i]	-52.6	70.30							
CCl_3OH	TVR [d]		73.59	18.93	21.35	22.99	24.14	25.60	26.51	27.82
(3)	I.R.[e]		3.84	1.71	1.60	1.48	1.37	1.24	1.16	1.08
	Total [f]	-65.01±2.25	77.43	20.64	22.95	24.47	25.51	26.84	27.67	28.90
	Schneider et al [g]	-70.0								
	Melius [h]	-66.20	79.2	20.19		24.02		26.68	27.54	28.92

a. Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm. One torsional frequency is excluded in the calculations of entropies and heat capacities. Instead, a more exact contribution from the hindered rotations about the C–O bond is included.
b. Units in kcal/mol.
c. Units in cal/mol/K.
d. The sum of contributions from translations, external rotations, and vibrations contribution from internal rotation about the C-O bond.
e. Symmetry number is taken into account (–Rln (symmetry number)).
f. Reference 6.
g. Reference 34.
h. Reference 5.

Table D-2 Ideal Gas-phase Thermodynamic Properties of Chlorinated Methyl Hydroperoxides [a]

Species and Symmetry No.		$\Delta H_f^\circ{}_{298}$ [b]	$S^\circ{}_{298}$ [c]	Cp300[c]	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
CH_2ClOOH	TVR [d]		68.16	13.34	16.16	18.60	20.59	23.54	25.65	28.92
(1)	I.R.[e]		6.84	4.63	4.74	4.72	4.67	4.44	4.09	3.16
	Total [f]	-41.40±1.45	76.40	17.97	20.90	23.32	25.26	27.98	29.74	32.08
	Knyazev et al. [g]	-36.59±3.97								
$CHCl_2OOH$	TVR [d]		74.50	16.85	19.75	22.03	23.77	26.20	27.83	30.25
(1)	I.R.[e]		7.11	5.37	5.39	5.08	4.70	4.06	3.57	2.73
	Total [f]	-44.71±3.25	83.16	22.22	25.14	27.11	28.47	30.26	31.40	32.98
	Knyazev et al. [g]	-39.96±3.39								
CCl_3OOH	TVR [d]		78.01	21.02	23.90	25.89	27.29	29.07	30.15	31.65
(3)	I.R.[e]		8.90	3.87	3.85	3.79	3.70	3.45	3.12	2.39
	Total [f]	-45.11±3.46	86.91	24.89	27.75	29.68	30.99	32.52	33.27	34.04
	Knyazev et al. [g]	-40.37±2.84								

a. Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm. R--OOH and RO--OH torsional frequencies are excluded in the calculations of entropies and heat capacities. Instead, a more exact contribution from hindered rotations about the C–O and O-O bonds is included.
b. Units in kcal/mol.
c. Units in cal/mol/K.
d. The sum of contributions from translations, external rotations, and vibrations. [e] Contribution from internal rotation about the C-O and O-O bonds.
e. Symmetry number is taken into account (–Rln(symmetry number)).
f. Reference 48.

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